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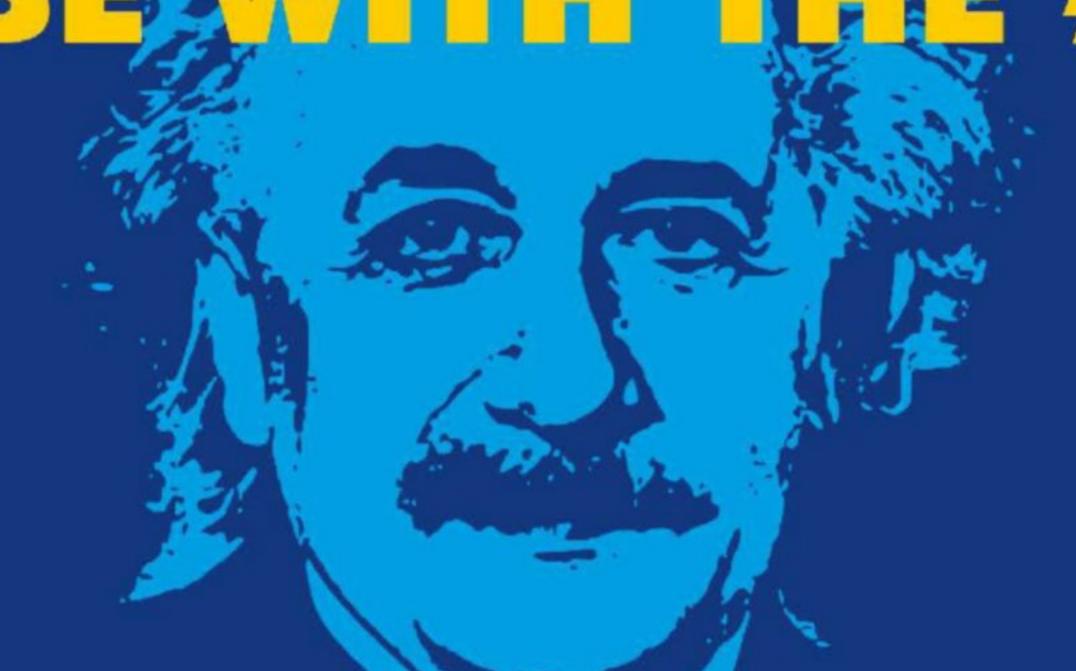
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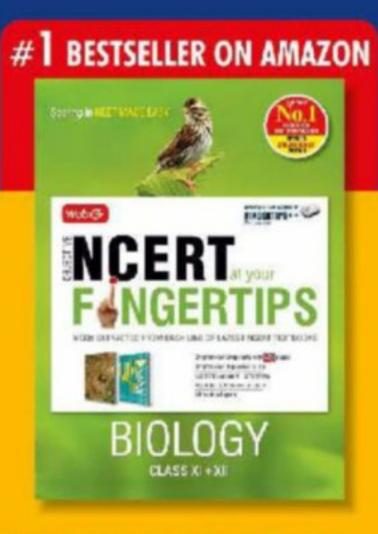


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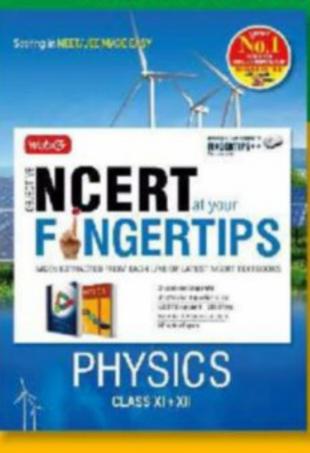
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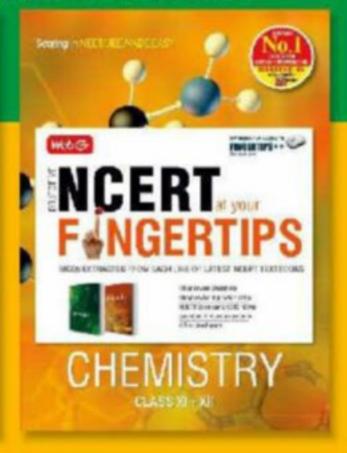


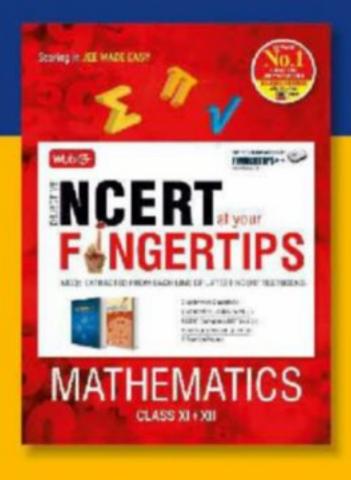
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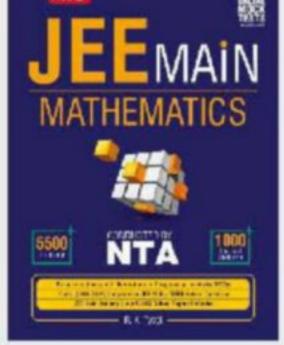


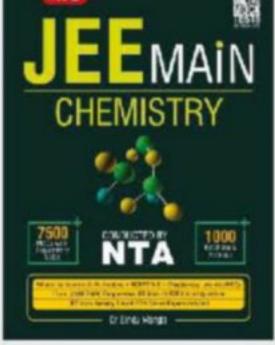


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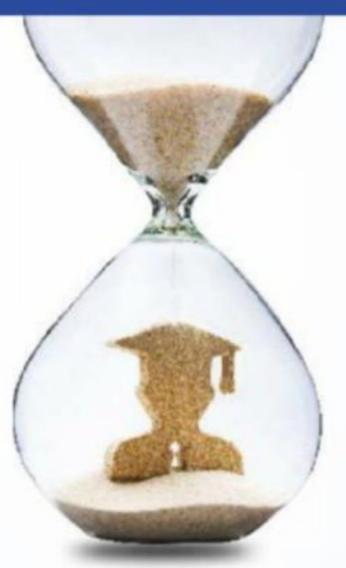
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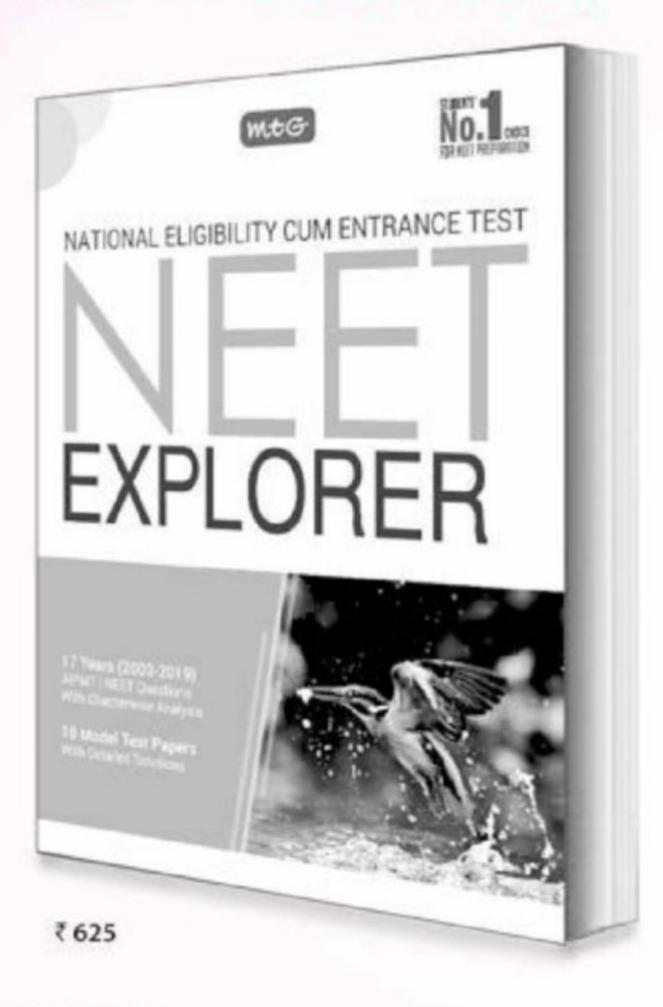
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# SET Class XI

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Which of the following is most stable enol form of the given compound?
 Generally commercial hydrochloric acid is prepared by heating NaCl with concentrated

- 2. Which of the following pairs can be distinguished by action of heat?
  - (i) K<sub>2</sub>CO<sub>3</sub> and CaCO<sub>3</sub>
  - (ii) Na<sub>2</sub>CO<sub>3</sub> and Mg(NO<sub>3</sub>)<sub>2</sub>
  - (iii) Mg(NO<sub>3</sub>)<sub>2</sub> and NaNO<sub>3</sub>
  - (a) Only (i) and (ii)
- (b) Only (i) and (iii)
- (c) (i), (ii) and (iii)
- (d) None of these

- Generally commercial hydrochloric acid is prepared by heating NaCl with concentrated H<sub>2</sub>SO<sub>4</sub>. How much H<sub>2</sub>SO<sub>4</sub> solution containing 93% H<sub>2</sub>SO<sub>4</sub> by mass is required for the production 1000 kg of concentrated hydrochloric acid containing 43% HCl by weight?
  - (a) 590.0 kg solution of H<sub>2</sub>SO<sub>4</sub>
  - (b) 310.3 kg solution of H<sub>2</sub>SO<sub>4</sub>
  - (c) 620.7 kg solution of H<sub>2</sub>SO<sub>4</sub>
  - (d) 708.2 kg solution of H<sub>2</sub>SO<sub>4</sub>
- 4. The major product for the following reaction is

(c) 
$$O_2N - O - CH_3$$
  
OH OH

(d) 
$$O_2N$$
  $\longrightarrow$   $O$   $\longrightarrow$   $OHOH$ 

1 mol N<sub>2</sub> and 4 mol H<sub>2</sub> are taken in 15 L flask at 27°C.

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

After complete conversion of N2 into NH3, 5 L of H<sub>2</sub>O is added. Pressure set up in the flask is

- (a)  $\frac{3 \times 0.0821 \times 300}{15}$  atm (b)  $\frac{2 \times 0.0821 \times 300}{10}$  atm
- (c)  $\frac{1 \times 0.0821 \times 300}{15}$  atm (d)  $\frac{1 \times 0.0821 \times 300}{10}$  atm
- When NaBH<sub>4</sub> is dissolved in water,
  - (a) Na<sup>+</sup> and BH<sub>4</sub> ions are formed which are stable.
  - (b) it evolve H<sub>2</sub> gas.
  - (c) NaOH and B<sub>2</sub>O<sub>3</sub> is formed.
  - (d) NaOH and H<sub>3</sub>BO<sub>3</sub> is formed.
- 7. Alkene (Z)  $\xrightarrow{O_3}$  CH<sub>3</sub>-C-Ph +
  O

  CH<sub>3</sub>-C-CH=O + CH<sub>3</sub>-CH=O

Alkene (Z) can be

- (a)  $CH_3 CH = CH Ph$  $CH_3-C-CH_3$
- (b) CH<sub>3</sub>-C-Ph  $CH_3-C-CH=CH-CH_3$
- (c)  $CH_3 C = CH Ph$  $CH_3-C=CH-CH_3$
- (d)  $Ph-C-CH=CH-CH_3$  $CH_3-C-CH_3$
- 8. Which of the following transition in hydrogen atom emits photon of maximum frequency?
  - (a) Second spectral line of Balmer series
  - (b) Second spectral line of Paschen series
  - (c) Fifth spectral line of Humphery series
  - (d) First spectral line of Lyman series.
- Which of the following should have pyramidal shape?
  - (a)  $[ClOF_2]^+$
- (b) ICl<sub>3</sub>
- (c) [BrICl]
- (d) All of these
- 10. For a hypothetical reversible reaction,  $1/2A_{2(g)} + 3/2B_{2(g)} \iff AB_{3(g)}$ ;  $\Delta H = -20$  kJ if standard entropies of  $A_2$ ,  $B_2$  and  $AB_3$  are 60, 40 and

- 50 JK<sup>-1</sup> mole<sup>-1</sup> respectively. The above reaction will be in equilibrium at
- (a) 400 K (b) 500 K (c) 250 K (d) 200 K
- 11. Which of the following have been arranged in order of decreasing oxidation number of sulphur?
  - (a)  $H_2S_2O_7 > Na_2S_4O_6 > Na_2S_2O_3 > S_8$
  - (b)  $SO > SO_4^{2-} > SO_3^{2-} > HSO_4^{-}$
  - (c)  $H_2S > SCl_2 > H_2SO_3 > H_2SO_5$
  - (d)  $H_2SO_4 > SO_2 > H_2S > H_2S_2O_8$
- 12. Which one of the following statements is correct?
  - (a) The elements having large negative values of electron gain enthalpy generally act as strong oxidising agents.
  - (b) The elements having low values of ionisation enthalpies act as strong reducing agents.
  - (c) The formation of  $S_{(g)}^{2-}$  from  $S_{(g)}$  is an endothermic process.
  - (d) All of the above.
- 13. If  $A \rightleftharpoons B(K_c = 3)$ ,  $B \rightleftharpoons C(K_c = 5)$ ,  $C \rightleftharpoons D(K_c = 2)$ The value of equilibrium constant for the above reaction are given, the value of equilibrium constant for  $D \rightleftharpoons A$  will be
  - (a) 15
- (b) 0.3
- (c) 30
- (d) 0.03
- 14. Which of the following statements is false?
  - (a) Absorption of the terrestrially radiated heat by the carbon dioxide is the main cause of global warming.
  - (b) Over Antarctica, the depletion of ozone layer is due to the formation of chlorine nitrate.
  - (c) The global warming of the earth surface is mainly due to reforestation.
  - (d) CO<sub>2</sub>, NO, CH<sub>4</sub>, O<sub>3</sub>, CCl<sub>4</sub> and water vapour are greenhouse gases.
- 15. Metals like Pt and Pd can take up large volume of hydrogen under special conditions. Hydrogen thus retained by the metal is called
  - (a) absorbed hydrogen(b) nascent hydrogen
  - (c) reactive hydrogen
- (d) occluded hydrogen.

#### SOLUTIONS

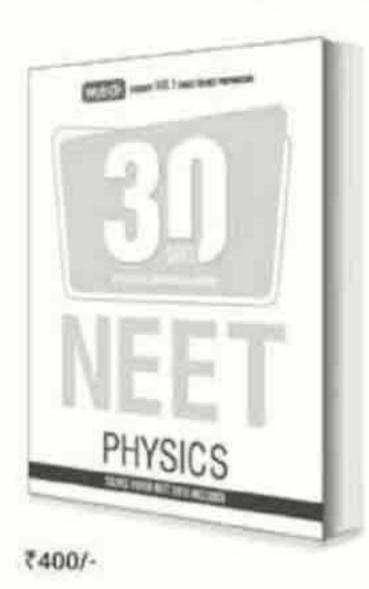
- (c): Repulsion between two C=C group of keto form is converted into more stabilized enol form by hydrogen bonding.
- 2. (c) : Na<sub>2</sub>CO<sub>3</sub> and  $K_2CO_3 \xrightarrow{\Delta}$  no reaction  $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

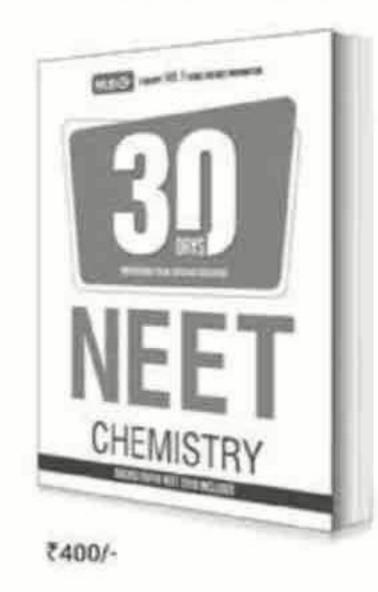


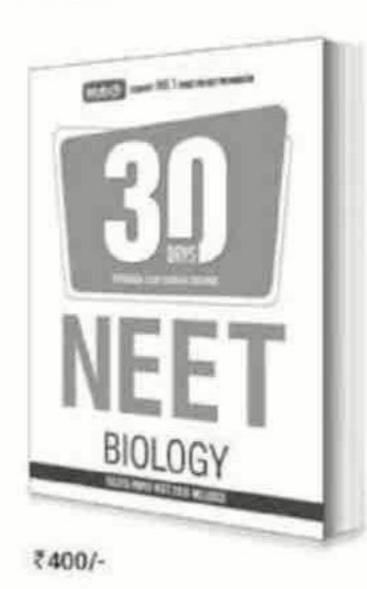
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$$Mg(NO_3)_2 \xrightarrow{\Delta} MgO + NO_2 + \frac{1}{2}O_2$$
  
 $NaNO_3 \xrightarrow{\Delta} NaNO_2 + \frac{1}{2}O_2$ 

3. (c) : 
$$2\text{NaCl} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl}$$
  
Mass of HCl =  $1000 \times \left(\frac{43}{100}\right) = 430 \text{ kg}$   

$$\frac{\text{Moles of HCl}}{2} = \frac{\text{Moles of H}_2\text{SO}_4}{1}$$

$$\Rightarrow \frac{430 \times 10^3}{36.5 \times 2} = \text{moles of H}_2\text{SO}_4$$
Mass of H<sub>2</sub>SO<sub>4</sub> =  $\frac{98 \times 430 \times 10^3}{36.5 \times 2} = 577.26 \times 10^3 \text{ g}$ 

4. (a):  $Br_2$  and  $H_2O$  gives HOBr

Mass of 93%  $H_2SO_4 = 577.26 \times \frac{100}{93} = 620.71 \text{ kg}$ 

$$O_2N - O - CH_2$$

$$O_2N - O - CH_3$$

$$O_2N - O - CH_3$$

5. (d): 
$$N_2 + 3H_2 \longrightarrow 2NH_3$$
  
 $t = 0$  1 mole 4 mole 0  
 $t = t_{final}$  0 1 mole 2 mole

 $NH_3$  will be absorbed by water and volume will be 15 - 5 = 10 L

$$P = \frac{nRT}{V} = \frac{1 \times 0.0821 \times 300}{10}$$
 atm

6. **(b)**: NaBH<sub>4</sub> + 2H<sub>2</sub>O  $\rightarrow$  NaBO<sub>2</sub> + 4H<sub>2</sub>  $\uparrow$ 

7. **(b)**:

CH<sub>3</sub>-C=
$$O+O+C$$
-C= $O+O+C$ -CH<sub>3</sub>

$$\begin{array}{c|c}
CH_3 & H \\
\hline
CH_3-C+O+C+C-C+O+CH-CH_3 \\
\hline
Doin by removing \\
O-atoms
\end{array}$$
Ph CH<sub>3</sub> H
$$\begin{array}{c|c}
CH_3 & H \\
\hline
CH_3-C=C-C=CH-CH_3 \\
\hline
CH_3-C=C-C=CH-CH_3
\end{array}$$

8. (d)

10. (b): 
$$\frac{1}{2}A_{(g)} + \frac{3}{2}B_{2(g)} \longrightarrow AB_{3(g)}$$
;  $\Delta H = -20 \text{ kJ}$   

$$\Delta S^{\circ} = \Sigma S_{P}^{\circ} - \Sigma S_{R}^{\circ} = 50 - \left(\frac{1}{2} \times 60 + \frac{3}{2} \times 40\right)$$

$$\Delta S^{\circ} = -40 \text{ JK}^{-1} \text{ mol}^{-1}$$
We know that,  $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ 
At equilibrium,  $\Delta G^{\circ} = 0$   $\therefore \Delta H^{\circ} = T\Delta S^{\circ}$ 

$$T = \frac{-20 \times 1000}{-40} = 500 \text{ K}$$

- 11. (a)
- **12. (d)**: (a) The elements having large negative values of electron gain enthalpy generally act as strong oxidising agents *e.g.*, halogens.
  - (b) The elements having low values of ionisation enthalpies act as strong reducing agents. *e.g.*, alkali metals.
  - (c) The formation of  $S_{(g)}^{2-}$  from  $S_{(g)}$  is an endothermic process as removal of electron will require energy.

13. (d): 
$$A \rightleftharpoons B$$
;  $K_{c_1} = \frac{[B]}{[A]} = 3$   
 $B \rightleftharpoons C$ ;  $K_{c_2} = \frac{[C]}{[B]} = 5$   
 $C \rightleftharpoons D$ ;  $K_{c_3} = \frac{[D]}{[C]} = 2$ ;  $A \rightleftharpoons D$ ;  $K_c = \frac{[D]}{[A]}$   
or  $K_c = K_{c_1} \times K_{c_2} \times K_{c_3} = 3 \times 5 \times 2 = 30$   
For  $D \rightleftharpoons A$ ;  $K'_c = \frac{[A]}{[D]}$ ;  $K'_c = \frac{1}{K_c} = \frac{1}{30} = 0.03$ 

- 14. (c)
- 15. (d): Metal like Pt and Pd, Ni etc. absorb large quantities of the gases, due to vacancies between these atom. This is called occlusion and hydrogen is called occluded hydrogen.

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2020

Unit 6

#### The p-Block Elements

#### Introduction

- Elements having outer electronic configuration of the type  $ns^2 np^1$  to  $ns^2 np^6$ , with all other inner orbitals completely filled, are termed as p-block elements. In other words, the elements in which the last electron enters into any of the outermost p-orbitals are called p-block elements. Thus, the general outer electronic configuration of the p-block elements is  $ns^2 np^{1-6}$ .
- The elements belonging to the group 13 to 18 of the long form of periodic table are p-block elements.
   The p-block elements include metals, non-metals and metalloids.

#### GROUP 13 ELEMENTS: BORON FAMILY

 Group 13 of the periodic table contains six elements, boron (B), aluminium (Al), gallium (Ga), indium (In), thallium (Tl) and Nihonium (Nh).

#### **Electronic Configuration**

• Their valence shell electronic configuration is  $ns^2np^1$ .

Element	Symbol	Electronic configuration [noble gas] $ns^2np^1$
Boron	<sub>5</sub> B	[He] $2s^22p^1$
Aluminium	<sub>13</sub> Al	[Ne] $3s^23p^1$
Gallium	31Ga	$[Ar]3d^{10}4s^24p^1$
Indium	<sub>49</sub> In	$[Kr]4d^{10}5s^25p^1$
Thallium	<sub>81</sub> Tl	$[Xe]4f^{14}5d^{10}6s^26p^1$
Nihonium	<sub>113</sub> Nh	$[Rn]5f^{14}6d^{10}7s^27p^1$

#### **General Physical Properties**

- Atomic radii and ionic radii :
  - Group 13 elements and their ions have smaller size than the corresponding group 2 elements because of the increase in nuclear charge.
  - Their atomic and ionic radii increase on going down the group with an exception at gallium.

Element	Metallic radius	Ionic radius		
	(Å)	$M^{3+}$ (Å)	$M^+$ (Å)	
В	0.885	0.27	-	
Al	1.43	0.535	_	
Ga	1.225	0.620	1.20	
In	1.67	0.800	1.40	
Tl	1.70	0.885	1.50	

#### Melting and boiling points:

 Melting points of group 13 elements do not vary regularly due to structural changes in the elements. The melting point decreases from B to Ga and then increases from Ga to Tl.

Element	Melting point (°C)	Boiling point (°C)
В	2300	2550
Al	660	2467
Ga	30	2240
In	157	2050
Tl	303	1470

 Boron shows a very high melting point because it exists as a giant covalent polymer crystal structure consisting of icosahedral units. • **Ionisation enthalpy:** The first ionisation enthalpy values of group 13 elements are lower than the corresponding alkaline earth metals, due to the fact that removal of electron is easy. [ns<sup>2</sup> np<sup>1</sup> configuration].

On moving down the group, *I.E.* decreases from B to Al, but the next element Ga has slightly higher ionisation enthalpy than Al due to the poor shielding of intervening *d*-electrons. It again decreases in In and then increases in the last element Tl.

#### Oxidation states :

Valence electronic configuration  $ns^2np^1$ , suggests that these elements are expected to show +1 and +3 oxidation states.

Element	Oxidation state
В	+3
Al	+1, +3
Ga	+1, +3
In	+1, +3
T1	+1, +3

- As we move down in the group, stability of +1 oxidation state increases due to the fact that the two s-electrons in the outer shell tend to remain paired and do not participate in bonding (inert pair effect).
- The stability of +3 oxidation state decreases from aluminium to thallium.

Thus, 
$$B^{3+} > Al^{3+} > Ga^{3+} > In^{3+} > Tl^{3+}$$
  
 $Tl^+ > In^+ > Ga^+ > Al^+ > B^+$   
 $Ga^{3+} > Ga^+$  while  $Tl^+ > Tl^{3+}$ 

#### Electropositive or metallic character :

- Group 13 elements are less electropositive than alkali metals and alkaline earth metals due to their higher ionisation energies.
- The electropositive character first increases down the group from boron to aluminium and then decreases from aluminium to thallium. Al shows higher metallic character than B due to its larger size and lower ionisation energy. Decrease in the electropositive character beyond Al is due to poor shielding by d-electrons, so that the valence electrons cannot be easily removed.
- Electropositive character can also be explained on the basis of their respective electrode potential.
- Because of high ionisation energy and small size, B is considered as non-metal.

#### Electronegativity:

- Group 13 elements are more electronegative than group 1 elements (alkali metals) and group 2 (alkaline earth metals).
- Electronegativity first decreases from B to Al and then increases due to poor shielding by d-electrons.

Element	В	Al	Ga	In	Tl
Pauling's	2.0	1.5	1.6	1.7	1.8
electronegativity					

#### TRENDS IN CHEMICAL PROPERTIES

#### Oxides and hydroxides :

All the elements of group 13 form oxides with formula  $M_2O_3$  and hydroxides with formula  $M(OH)_3$ . Reactivity of these elements towards oxygen increases down the group.

Oxides	Hydroxides	Nature
$B_2O_3$	B(OH) <sub>3</sub>	acidic
Al <sub>2</sub> O <sub>3</sub>	Al(OH) <sub>3</sub>	amphoteric
Ga <sub>2</sub> O <sub>3</sub>	Ga(OH) <sub>3</sub>	amphoteric
In <sub>2</sub> O <sub>3</sub>	In(OH) <sub>3</sub>	basic
$Tl_2O_3$	Tl(OH) <sub>3</sub>	strongly basic

As we moves down the group, the atomic size of elements goes on increasing whereas, the ionisation energy decreases. As a result, the strength of M – O bond goes on decreasing accounting for the increase in basic character down the group or conversely explains the decrease in acidic character.

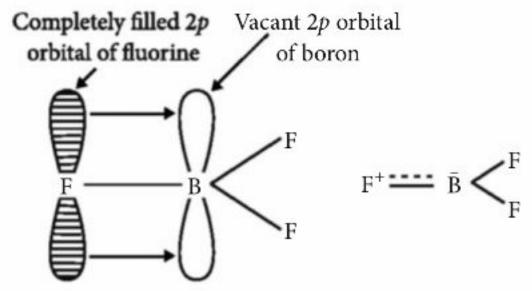
- Halides: Group 13 elements form trihalides(MX<sub>3</sub>).
   Monohalides of thallium are also given as TlF, TlCl,
   TlBr and TlI.
  - Due to small size and high electronegativity, all boron halides are covalent and sp<sup>2</sup> hybridised.
  - Boron halides BX<sub>3</sub> are electron deficient compounds having six electrons in the outermost orbit thus function as Lewis acid by accepting a pair of electrons.

$$BX_3 + NH_3 \longrightarrow \{H_3N \rightarrow BX_3\}$$

The Lewis acid strength follows the order:

$$BF_3 < BCl_3 < BBr_3 < BI_3$$

This order can be explained on the basis of back bonding or back donation. In  $BF_3$ , there is donation of electron from unutilized 2p-orbitals of fluorine to a vacant 2p-orbital of B.

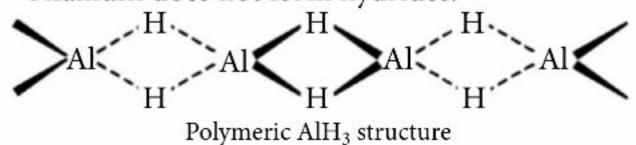


Thus, B-F bond has some double bond character.

- Lewis acid character of halides of group 13 elements decreases in the order :  $BX_3 > AlX_3 > GaX_3 > InX_3$ 

#### Formation of hydrides :

- None of the group 13 elements reacts directly with hydrogen. However a number of hydrides of these elements are known.
- Boron forms a number of stable covalent hydrides with general formula B<sub>n</sub>H<sub>n+4</sub> (nidoboranes e.g., B<sub>2</sub>H<sub>6</sub>) and B<sub>n</sub>H<sub>n+6</sub> (arachnoboranes e.g., B<sub>4</sub>H<sub>10</sub>). These are called boranes and are electron deficient compounds.
- The simplest and most important boron hydride is diborane (B<sub>2</sub>H<sub>6</sub>).
- Other members of this group also form a stable hydride but they are polymeric in nature e.g., (AlH<sub>3</sub>)<sub>n</sub>, (GaH<sub>3</sub>)<sub>n</sub>, (InH<sub>3</sub>)<sub>n</sub> and contain M H<sub>b</sub> M bridge bond. Their stability decreases as we move down the group due to corresponding decrease in strength of M H bond as the size of atom increases.
- Thallium does not form hydrides.



#### • Formation of carbides :

 Boron and aluminium on heating with carbon at high temperature form carbides.

$$4B + C \xrightarrow{2500^{\circ}C} B_4C, 4Al + 3C \xrightarrow{1000^{\circ}C} Al_4C_3$$

- Boron carbide is covalent in nature.
- Aluminium carbide is ionic carbide. On hydrolysis it gives methane, hence it is sometimes called as aluminium methanide.
   Al<sub>4</sub>C<sub>3</sub> + 12H<sub>2</sub>O → 4Al(OH)<sub>3</sub> + 3CH<sub>4</sub>↑

#### **Anomalous Properties of Boron**

• Due to the smallest size, high ionisation energy, absence of vacant *d*-orbitals and high electronegativity boron shows anomalous behaviour as compared to other members of the group.

Property	Boron	Other elements of group 13
Metallic behaviour	Non-metal	Metals
Maximum covalency	4	6
Allotropy	Exhibits	Do not exhibit
Oxidation states	Only +3	+1, +3
Compounds	Only covalent	Both ionic and covalent
Halides	Monomeric	Polymeric
Aqueous solution	No ionisation	Form cations
Oxides and hydroxides	Acidic	Amphoteric or basic
Action of non- oxidising acids	No action	React
Combination with metals	Forms boride	Do not combine (form alloy)

#### PEEP INTO PREVIOUS YEARS

1. Which one of the following elements is unable to form  $MF_6^{3-}$  ion?

(a) Ga

- (b) Al
- (c) B
- (d) In

(NEET 2018)

2. Consider the following standard electrode potentials  $(E^{\circ} \text{ in volts})$  in aqueous solution,

<b>Element</b>	$M^{3+}/M$	$\underline{M}^+/\underline{M}$
A1	-1.66	+0.55
Tl	+1.26	-0.34

Based on these data, which of the following statements is correct?

- (a) Tl<sup>+</sup> is more stable than Al<sup>+</sup>.
- (b)  $Tl^{3+}$  is more stable than  $Al^{3+}$ .
- (c) Al<sup>+</sup> is more stable than Al<sup>3+</sup>.
- (d) Tl<sup>+</sup> is more stable than Al<sup>3+</sup>.

(JEE Main Online 2017)

- The increasing order of atomic radii of the following group 13 elements is
  - (a) Al < Ga < In < Tl
- (b) Ga < Al < In < Tl
- (c) Al < In < Ga < Tl
- (d) Al < Ga < Tl < In

(JEE Advanced 2016)

#### SOME IMPORTANT COMPOUNDS OF GROUP 13 ELEMENTS

	Preparation	Properties	Structure
Borax (Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> .10H <sub>2</sub> O)	Ca <sub>2</sub> B <sub>6</sub> O <sub>11</sub> + 2Na <sub>2</sub> CO <sub>3</sub> $\xrightarrow{\Delta}$ Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> + 2NaBO <sub>2</sub> + 2CaCO <sub>3</sub> Colemanite 4NaBO <sub>2</sub> + CO <sub>2</sub> $\longrightarrow$ Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> + Na <sub>2</sub> CO <sub>3</sub> 4H <sub>3</sub> BO <sub>3</sub> + Na <sub>2</sub> CO <sub>3</sub> $\xrightarrow{\Delta}$ Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> + 6H <sub>2</sub> O + CO <sub>2</sub> Uses:	$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10H_2O$ $Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$ Transparent glassy bead $Na_2B_4O_7 + 2NaOH \longrightarrow 4NaBO_2 + H_2O$ $Na_2B_4O_7 + H_2SO_4 \longrightarrow Na_2SO_4$ $+ H_2B_4O_7$	2Na <sup>+</sup> O- OH OH OH OH
<b>B</b>	<ul> <li>It is used as water softener an</li> <li>In the laboratory it is used for</li> </ul>		
Orthoboric acid (H <sub>3</sub> BO <sub>3</sub> )	$4H_3BO_3 + 2NaCl$ $Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow$ $4H_3BO_3 + Na_2SO_4$ $Ca_2B_6O_{11} + 4SO_2 + 11H_2O \longrightarrow$ $2Ca(HSO_3)_2 + 6H_3BO_3$ $B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$ $BN + 3H_2O \longrightarrow H_3BO_3 + NH_3$ Uses: • It is used in the manufacture	$H_3BO_3 \xrightarrow{370 \text{ K}} HBO_2 + H_2O$ $\downarrow^{410 \text{ K}} H_2B_4O_7$ $\downarrow^{\text{Red heat}}$ $2B_2O_3 + H_2O$ $Core H_2SO_4$	HOBOHOHOHOHOHOHOHOHOHOHOHOHOHOHOHOHOHOH
Diborane (B <sub>2</sub> H <sub>6</sub> )	$6NaF$ $4BF_3.Et_2O + 3LiAlH_4 \xrightarrow{Diethyl} \bullet$ $2B_2H_6 + 3LiF + 3AlF_3 + 4Et_2O$	$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$ $B_2H_6 + 6CH_3OH \longrightarrow 2B(OCH_3)_3 + 6H_2$ $B_2H_6 + 2NaH \xrightarrow{Diethyl} 2NaBH_4$	H B 120° H 178 pm

#### Uses:

- It is used for preparing a number of borohydrides such as LiBH<sub>4</sub>, NaBH<sub>4</sub>, etc.
- It is used as a reducing agent in organic reactions.

$$2Al + 3Cl2 \longrightarrow 2AlCl3$$

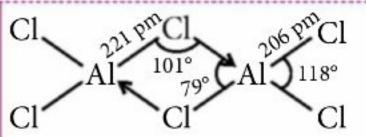
$$2Al + 6HCl \longrightarrow 2AlCl3 + 3H2$$

$$Al2O3 + 3C + 3Cl2 \xrightarrow{100^{\circ}C}$$

$$2AlCl3 + 3CO$$

Anhydrous AlCl<sub>3</sub> fumes in moist air due Cl to hydrolysis and the resulting solution is acidic.

AlCl<sub>3</sub> + 3H<sub>2</sub>O 
$$\longrightarrow$$
 Al(OH)<sub>3</sub> + 3HCl  
AlCl<sub>3</sub>+3NH<sub>4</sub>OH  $\longrightarrow$  Al(OH)<sub>3</sub>\(\psi + 3NH<sub>4</sub>Cl  
Gelatinous ppt.  
(Insoluble in excess NH<sub>4</sub>OH)  
AlCl<sub>2</sub> + 3NaOH  $\longrightarrow$  Al(OH)<sub>2</sub>\(\psi



#### Uses:

Aluminium chloride

(AICI3)

Anhydrous AlCl<sub>3</sub> is used as a catalyst in Friedel-Craft's reaction and in cracking of petroleum.

#### PEEP INTO PREVIOUS YEARS

- Diborane (B<sub>2</sub>H<sub>6</sub>) reacts independently with O<sub>2</sub> and H<sub>2</sub>O to produce, respectively

  - (a)  $HBO_2$  and  $H_3BO_3$  (b)  $B_2O_3$  and  $H_3BO_3$

  - (c)  $B_2O_3$  and  $[BH_4]^-$  (d)  $H_3BO_3$  and  $B_2O_3$

(JEE Main 2019)

- 5. The green colour produced in the borax bead test of a chromium(III) salt is due to

  - (a) CrB (b)  $Cr_2O_3$
  - (c)  $Cr(BO_2)_3$
- (d)  $Cr_2(B_4O_7)_3$

(JEE Advanced 2019)

- Boric acid is an acid because its molecule
  - (a) contains replaceable H<sup>+</sup> ion
  - (b) gives up a proton
  - (c) accepts OH<sup>-</sup> from water releasing proton
  - (d) combines with proton from water molecule.

(NEET Phase-II 2016)

#### Points For Extra Scoring

- Gallium is a low melting solid (m.pt =  $29.8^{\circ}$ C) and readily supercools i.e., remains liquid even at temperatures several degrees below its melting point.
- Boron nitride has a layer structure resembling graphite, in which hexagonal ring consists of alternating of boron and nitrogen atoms.
- Corundum (an  $\alpha$ -form of Al<sub>2</sub>O<sub>3</sub>) an extremely hard substance is used as jeweller's rouge to polish glass.

- Boron halides do not exist as dimer due to small size of boron atom which makes it unable to coordinate four large-sized halide ions.
- In thallium triiodide ( $TlI_3$ ), thallium is in (+1) oxidation state and anion is  $I_3^-$ .
- Thallium is the highly toxic element amongst the group 13 members.
- The anhydrous alum is called burnt alum.

#### GROUP 14 ELEMENTS: CARBON FAMILY

Group 14 of the periodic table contains six elements, carbon (C), silicon (Si), germanium (Ge), tin (Sn), lead (Pb) and Flerovium (Fl).

#### **Electronic Configuration**

Their valence shell electronic configuration is  $ns^2np^2$ .

Element	Symbol	Electronic configuration [noble gas] ns <sup>2</sup> np <sup>2</sup>
Carbon	<sub>6</sub> C	[He] $2s^22p^2$
Silicon	<sub>14</sub> Si	[Ne] $3s^23p^2$
Germanium	<sub>32</sub> Ge	[Ar] $3d^{10}4s^24p^2$
Tin	<sub>50</sub> Sn	[Kr] $4d^{10}5s^25p^2$
Lead	<sub>82</sub> Pb	[Xe] $4f^{14}5d^{10}6s^26p^2$
Flerovium	<sub>114</sub> Fl	[Rn] $5f^{14}6d^{10}7s^27p^2$

#### **General Physical Properties**

- Atomic radii:
  - The atomic radii of group 14 elements are smaller than those of corresponding elements

of group 13, because as we move from left to right in a period, effective nuclear charge increases, consequently, the size of the atom decreases.

 The atomic radii of group 14 elements increase regularly on moving down the group mainly due to increase in the number of shells.

#### • Melting and boiling points :

- The melting and boiling points of group 14 elements are much higher than those of the elements of group 13. It is because these form four covalent bonds with each other and hence there exists strong binding forces between their atoms both in the solid as well as in the liquid state.
- The melting and boiling points decrease on descending the group from carbon to lead because the M-M bond becomes weaker as the atom size increases.

#### Ionization enthalpy:

- The first ionization potential of group 14 elements are higher than those of corresponding elements of group 13 due to increased nuclear charge.
- Due to increase in the atomic radii of these elements from C to Pb the ionisation enthalpy decreases on moving down the group.
- Due to ineffective shielding of valence electrons by d- and f-orbitals the sequence for ionization energy is

C > Si > Ge > Sn < Pb

#### Oxidation state :

Element	Oxidation state
С	+4
Si	+4
Ge	+2, +4
Sn	+2, +4
Pb	+2, +4

The stability of +2 state increases from Ge to Pb, *i.e.*,  $Ge^{2+} < Sn^{2+} < Pb^{2+}$  but for +4 oxidation state it is  $Ge^{4+} > Sn^{4+} > Pb^{4+}$ .

As we move down, inert pair effect increases and stability of lower oxidation state increases.

 $Pb^{2+} > Pb^{4+}, Ge^{4+} > Ge^{2+}, Sn^{4+} > Sn^{2+}$ 

Electropositive character or metallic character:
 Group 14 elements are less electropositive than group 13 elements.

Element	Metallic character	
С	Non-metal	
Si	Non-metal	
Ge	Metalloid	
Sn	Metal	
Pb	Metal	

#### Catenation (Tendency to form chains):

- Catenation is the property of elements to form long chains or rings by self-linking of their own atoms through covalent bonds.
- The tendency for catenation decreases in the order C>> Si > Ge ≈ Sn>> Pb
- Carbon shows a remarkable catenation due to smaller size and high electronegativity, so that C-C bond is extremely stable.
- Allotropy: All the elements of group 14 except Pb show allotropy.

#### CHEMICAL PROPERTIES

- Hydrides: All members of the group form covalent hydrides. Their number and ease of formation decreases down the group. Hydrides of carbon are called hydrocarbons (alkanes, alkenes or alkynes). Hydrides of Si and Ge are known as silanes and germanes. The only hydrides of Sn and Pb are SnH<sub>4</sub> (stannane) and PbH<sub>4</sub> (plumbane).
  - Their thermal stability decreases down the group.
  - Their reducing character increases down the group.
- Halides: All the elements give tetrahedral and covalent halides of the type MX<sub>4</sub> except PbBr<sub>4</sub> and PbI<sub>4</sub>.

Thermal stability :  $CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$ Order of thermal stability with common metals :

 $MF_4 > MCl_4 > MBr_4 > MI_4$ 

Except  $CX_4$  other tetrahalides can hydrolysed due to the presence of vacant d-orbitals.

 $SiX_4 + 2H_2O \longrightarrow SiO_2 + 4HX$ 

Ease of hydrolysis :  $SiX_4 > GeX_4 > SnX_4 > PbX_4$ 

 Oxides: They form two type of oxides, monooxides of the type MO and dioxides of the type MO<sub>2</sub>.

SiO<sub>2</sub> is a solid with three dimensional network in which Si is bonded to four oxygen atoms tetrahedrally and covalently.

#### Carbides :

- The binary compounds of carbon with elements other than hydrogen are called *carbides*.
- Ionic carbides are formed by the most electropositive metals such as alkali and alkaline earth metals and Al.
- Both Be<sub>2</sub>C and Al<sub>4</sub>C<sub>3</sub> are called methanides because they react with H<sub>2</sub>O yielding methane.
- Covalent carbides are formed by Si and B.
- SiC (carborundum) has a diamond like structure, hence it is called artificial diamond.
- Interstitial carbides are formed by transition elements in which C-atoms occupy interstitial positions in the close-packed arrays of metal atoms. W, Zr, Ti, Ta and Mo can form interstitial carbides.

#### **Allotropes of Carbon**

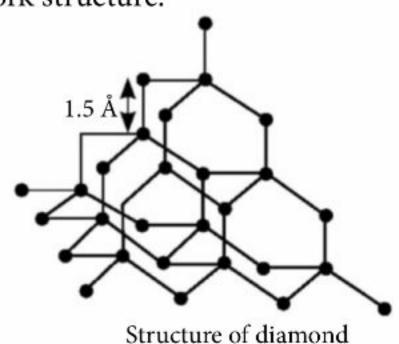
- The allotropic forms of carbon are:
  - Crystalline form : diamond and graphite.
  - Amorphous form : coal, charcoal, lampblack, etc.

#### Diamond:

- It is a transparent, crystalline substance with very high refractive index.
- It is the purest form of carbon found naturally and can also be made artificially.
- Diamond is the hardest natural substance known and is a bad conductor of electricity.

#### Structure:

- Each carbon atom of diamond is bonded to four other carbon atoms, through sp<sup>3</sup> hybridised orbitals, situated at the corners of a regular tetrahedron, with C C bond cluster of 1.54 Å and bond angle of 109.5°.
- This gives diamond a three-dimensional network structure.

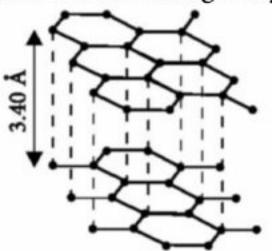


#### Graphite:

- It is a dark grey, crystalline solid which is soft and greasy to touch. It possesses a metallic lustre.
- It is also known as 'plaumbago' (black lead) as it leaves a black mark on paper.
- It is a good conductor of electricity and its conductivity increases with rise in temperature.

#### Structure:

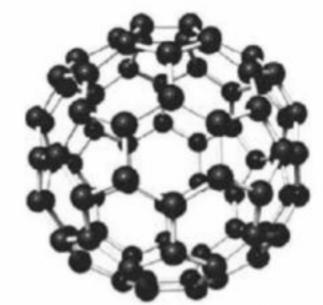
- It has a two dimensional sheet like structure with each carbon atom being covalently bonded to three carbon atoms through sp<sup>2</sup> hybridised orbitals, forming a planar hexagonal structure.
- The fourth electron of each carbon forms a pi(π) bond with partial overlap with that of the neighbouring carbon.
- The C C bond length is 1.42 Å, shorter than that in diamond. The π-electrons are free to move (mobile electrons) and account for the electrical conductivity.
- The adjacent hexagonal layers (sheets) are held by weak van der Waals' forces thus, making it easy for the layers to slide over one another, accounting for its soft and greasy texture.



Structure of graphite

#### **Fullerenes**

- Fullerenes are made by heating graphite in an electric arc in the presence of inert gases such as helium or argon. Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds. Fullerenes are cage like molecules. C<sub>60</sub> molecule has a shape like soccer ball and called Buckminsterfullerene.
- It contains twenty, six-membered rings and twelve, five-membered rings. A six membered ring is fused with six or five membered ring but a five membered ring can only be fused with six membered ring. All the carbon atoms are equal and they undergo  $sp^2$  hybridisation. This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C–C distances of 143.5 pm and 138.3 pm, respectively. Spherical fullerenes are also called bucky balls in short.



Structure of Buckminsterfullerene

#### **Anomalous Properties of Carbon**

Carbon differs from other elements of group 14 because of its smaller size, high electronegativity, absence of d-orbitals and high tendency of catenation.

Property	Carbon	Other elements
Hardness	hardest (diamond)	less hard
M.pt. and B.pt.	high	low
Maximum covalency	4	6
Multiple bonds	$p\pi$ - $p\pi$ (high extent)	$p\pi$ - $d\pi$ (low extent)
Catenation	very high tendency	very low
Tetrahalides	does not undergo hydrolysis	undergo hydrolysis

#### PEEP INTO PREVIOUS YEARS

- 7. Which of the following is incorrect statement?
  - (a)  $SnF_4$  is ionic in nature.
  - (b) PbF<sub>4</sub> is covalent in nature.
  - (c) SiCl<sub>4</sub> is easily hydrolysed.
  - (d)  $GeX_4$  (X = F, Cl, Br, I) is more stable than  $GeX_2$ . (NEET 2019)
- **8.** A tin chloride 'Q' undergoes the following reactions (not balanced)

$$Q + Cl^- \rightarrow X$$

$$Q + Me_3N \rightarrow Y$$

$$Q + CuCl_2 \rightarrow Z + CuCl$$

X is monoanion having pyramidal geometry. Both Y and Z are neutral compounds. Choose the correct option(s).

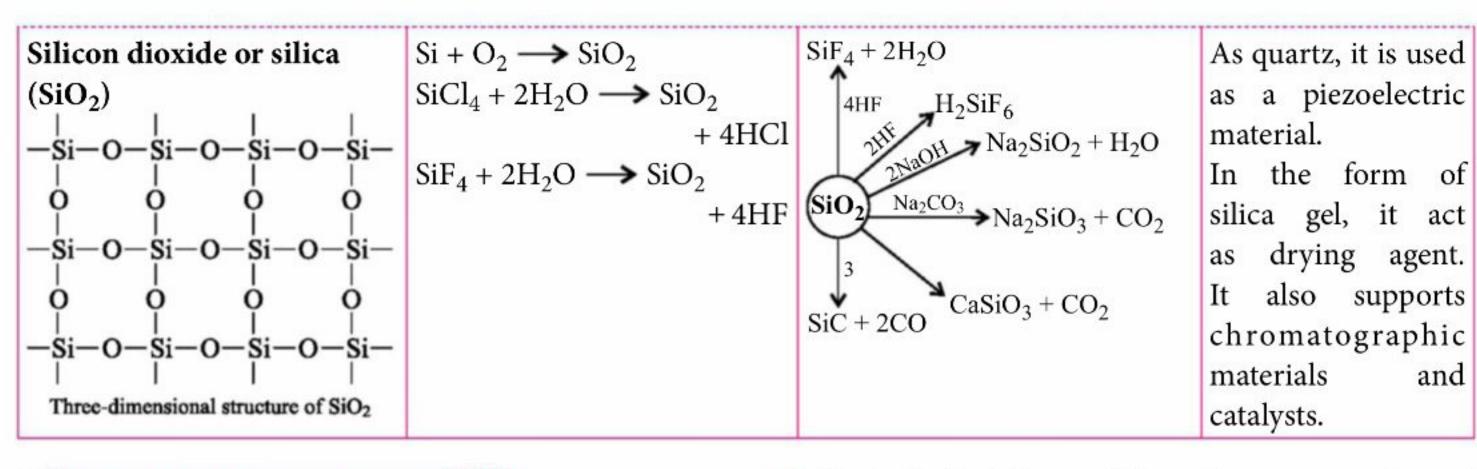
- (a) The central atom in X is  $sp^3$  hybridized.
- (b) There is a coordinate bond in Y.
- (c) The oxidation state of the central atom in Z is +2.
- (d) The central atom in Z has one lone pair of electrons. (JEE Advanced 2019)
- 9. In graphite and diamond, the percentage of *p*-characters of the hybrid orbitals in hybridisation are respectively
  - (a) 33 and 75
- (b) 50 and 75
- (c) 33 and 25
- (d) 67 and 75

(JEE Main Online 2018)

#### Some Important Compounds of Group 14 Elements

Compound Preparation		Properties	Uses	
Carbon monoxide (CO)  :C≡O:+ ↔ :C=Ö:  or :C≝O:	*	It is neutral towards litmus.  It is colourless odourless and tasteless neutral oxide.  2CO <sub>2</sub> COCl <sub>2</sub> (Phosgene)  2Fe + 3CO <sub>2</sub> 2Fe + 3CO <sub>2</sub>	producer gas $(N_2 + CO)$ and water gas $(H_2 + CO)$ , it is used as fuel.	
	obtained as water gas $(H_2 + CO)$ and producer gas $(CO + N_2)$ . $C_{(s)} + H_2O_{(g)} \xrightarrow{200-1000^{\circ}C}$ $CO_{(g)} + H_{2(g)}$ Water gas	1012 1012	In the metallurgy of nickel. As a reducing agent. For the manufacture of methyl alcohol and synthetic petrol	

Silicones (Si $-O-Si$ ) linkage ( $R_2SiO$ ) <sub>n</sub> $-O-Si-O-Si-O-Si$ $-O-Si-O-Si-R-N$ $-O-R-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N-N$	Dialkyldichloro silane $R_2 \text{SiCl}_2 \xrightarrow{+2H_2O} R_2 \text{Si(OH)}_2$ Dialkyldihydro silane $-H_2O \text{Polymerisation}$ $\begin{bmatrix} R & R \\ -O-\text{Si}-O-\text{Si}-O \\ R & R \end{bmatrix}_n$ Silicone	Silicone polymers are highly stable towards heat. High dielectric strength. Polymers of silicon with low molecular weight are soluble in organic solvents.  They are not affected by weak acids, alkalies, salt solutions and resistant to oxidation.  They are water repellents and good electrical insulators.	are used as sealant, greases, varnishes and these can be used even at very low temperatures (of the order of -40°C). These are used as lubricants at both high and low temperatures. Silicone rubbers are very useful because they retain their elasticity at lower temperatures as compared to other rubbers. They are also mixed in paints to make them damp resistant.
Carbon dioxide (CO <sub>2</sub> ) $: \ddot{O} = C = \ddot{O}:^{+} \longleftrightarrow ^{+}O \equiv C - O:$ $\longleftrightarrow ^{-}O - C \equiv O^{+}$	$ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$ $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$ $NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 +$ $CO_2 \uparrow + H_2O$	$(C_6H_{10}O_5)_x + xO_2$ $(Starch)$ $(Sodium carbonate)$ $(C_6H_{10}O_5)_x + xO_2$ $(Starch)$	In aerated waters, e.g., in soda water, etc.  CO <sub>2</sub> is used in extinguishing fire.  Solid carbon dioxide (dry ice) is used as refrigerant.  In the manufacture of sodium carbonate and sodium bicarbonate by the Solvay's process.



#### PEEP INTO PREVIOUS YEARS

- 10. Which of the following compounds is used in cosmetic surgery?
  - (a) Silica
- (b) Silicates
- (c) Silicones
- (d) Zeolites

(Odisha NEET 2019)

- 11. Lithium aluminium hydride reacts with silicon tetrachloride to form
  - (a) LiCl, AlCl<sub>3</sub> and SiH<sub>4</sub>
  - (b) LiCl, AlH<sub>3</sub> and SiH<sub>4</sub>
  - (c) LiH, AlCl<sub>3</sub> and SiCl<sub>2</sub>
  - (d) LiH, AlH<sub>3</sub> and SiH<sub>4</sub>

(JEE Main Online 2018)

- 12. Under hydrolytic conditions, the compounds used for preparation of linear polymer and for chain termination, respectively, are
  - (a) CH<sub>3</sub>SiCl<sub>3</sub> and Si(CH<sub>3</sub>)<sub>4</sub>
  - (b) (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub> and (CH<sub>3</sub>)<sub>3</sub>SiCl
  - (c) (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub> and CH<sub>3</sub>SiCl<sub>3</sub>
  - (d) SiCl<sub>4</sub> and (CH<sub>3</sub>)<sub>3</sub>SiCl (*JEE Advanced 2015*)

#### Points For Extra Scoring

- Graphite can be converted into diamond at  $\approx 55 \times 10^3$  atmospheric pressure.
- Chemical composition of ordinary glass is  $Na_2SiO_3 \cdot CaSiO_3 \cdot 4SiO_2$ .
- PbO is called litharge, Red lead (Pb3O4) is a mixed oxide.

#### **Answer Key For Peep Into Previous Years**

(a,b)

- **(b)**

(d)

**(b)** 

(c)

- (c)
- (c) (b)
- WRAP it up!
- 1. AlCl<sub>3</sub> is an electron deficient compound but AlF<sub>3</sub> is not. This is because
  - (a) atomic size of F is smaller than Cl which makes AlF<sub>3</sub> more covalent
  - (b) AlCl<sub>3</sub> is a covalent compound while AlF<sub>3</sub> is an ionic compound
  - (c) AlCl<sub>3</sub> exists as a dimer but AlF<sub>3</sub> does not
  - (d) Al in AlCl<sub>3</sub> is in sp<sup>3</sup> hybrid state but Al in AlF<sub>3</sub> is in  $sp^2$  state.
- 2. Aqueous solution of borax acts as a buffer because
  - (a) it contains weak acid and its salt with strong base

- (b) it contains tribasic acid and strong base
- (c) it contains number of neutral water molecules
- (d) none of these.
- Borosilicate glass has the special property of being
  - (a) transparent
- (b) uncrackable
- (c) resistant of heat
- (d) tough
- Which of the following exists in gaseous form in nature?
  - (a) ClF<sub>3</sub>
- (b) BF<sub>3</sub>
- (c) IF<sub>3</sub>
- (d) ICl

- 5. Pb + conc.  $HNO_3$  gives
  - (a)  $Pb(NO_3)_2 + NO_2$ 
    - (b)  $PbNO_3 + NO$
  - (c)  $Pb(NO_3)_4 + NO_3$  (d)  $Pb(NO_3)_3 + N_2O$
- **6.** A solid element (symbol *Y*) conducts electricity and forms two chlorides  $YCl_n$  (a colourless volatile liquid) and  $YCl_{n-2}$  (a colourless solid). To which one of the following groups of the periodic table does Y belong?
  - (a) 13
- (b) 14
- (c) 15
- (d) 16
- 7. An element of group 14 forms two oxides one of which is highly poisonous and neutral. Other oxide can be easily liquefied and compressed to give a solid which is used as a refrigerant under the name of drikold. The element and the oxides are
  - (a) Si, SiO, SiO<sub>2</sub>
- (b) Pb, PbO, PbO<sub>2</sub>
- (c) C, CO, CO<sub>2</sub>
- (d) Sn, SnO, SnO<sub>2</sub>
- Which of the following statement about group IV elements (C to Pb) is not correct?
  - (a) Sn and Pb form dichlorides
  - (b) The thermal stability of hydrides decreases from CH<sub>4</sub> to PbH<sub>4</sub> as bond enthalpy for M — H bond decreases.
  - (c) All form tetrafluorides, tetrachlorides.
  - (d) All form tetraiodides.

- 9. Which one of the following has the highest Lewis acid strength?
  - (a)  $BI_3$
- (b) BBr<sub>3</sub>
- (c)  $BF_3$
- (d) BCl<sub>3</sub>
- 10. When bauxite powder is mixed with coke and reacted with nitrogen at 2075 K, carbon monoxide and *X* are formed. What is the gas formed when *X* is reacted with water?
  - (a)  $NH_3$
- (b) N<sub>2</sub>
- (c)  $N_2O$
- (d)  $O_2$
- 11. Which of the following is strongest bond?
  - (a) Si Si
- (b) C C
- (c) Sn Sn
- (d) Pb Pb
- 12. When NaOH solution is added to AlCl<sub>3</sub> solution, a white ppt. first appears which dissolves in excess of NaOH. In the solution so obtained
  - (a) aluminium ion is present in anion
  - (b) aluminium ion is present in cation
  - (c) aluminium ion is present in both the ions
  - (d) aluminium is present in neither the cation nor the anion.
- 13. Iodine oxidises sodium borohydride to give
  - (a)  $B_2H_6$
- (b) sodium hydride
- (c) HI
- (d)  $I_3^-$
- 14. In the manufacture of cement which of the following is used?

Unscramble the words given in column I and match them with their explanations in column II.

#### Column I

- **TESOROEC**
- PASTSELATHI
- **PXECILEX**
- **TAGCYUFI**
- LMULIET
- **ROXATOHNL**
- NATPAI
- RAPSILECE

#### Column II

- A molecular charge transfer complex formed by the complexing of a donor in an excited state with an acceptor in its ground state.
- Used in the measure of effective pressure dependence versus the chemical potential of a gas.
- Fractions obtained in the distillation of coal or wood tar.
- The decorative and corrosion-resistant surface given to bronze, iron, etc., as an oxide film formed on warming the metal.
- MgO either natural or formed by heating Mg(OH)<sub>2</sub> used in furnace linings.
- Naturally occurring, hard bitumens of high purity containing only 1-2% of mineral matter.
- Reduction product of anthraquinone.
- Al<sub>6</sub>Si<sub>2</sub>O<sub>13</sub>, the stablest aluminum silicate, formed by heating other aluminosilicates used in refractories and glasses.

Readers can send their responses at editor@mtg.in or post us with complete address by 10<sup>th</sup> of every month. Names of solution senders will be published in next issue.

- (a) Clay and silica
- (b) Limestone and silica
- (c) Limestone and clay (d) Limestone and gypsum.
- **15.** Which is not correct?
  - (a) GeO<sub>2</sub> is weakly acidic.
  - (b) GeCl<sub>4</sub> forms [GeCl<sub>2</sub>]<sup>2-</sup> ion with HCl.
  - (c) Ge(OH)<sub>2</sub> is amphoteric.
  - (d) GeCl<sub>2</sub> is more stable than GeCl<sub>4</sub>.
- **16.** The products of the following reaction are  $SiO_2 + C \xrightarrow{\Delta}$ 
  - (a) SiC and CO<sub>2</sub>
- (b) SiO and CO
- (c) SiC and CO
- (d) Si and CO<sub>2</sub>
- 17. Which of the following statements is not true both for B and Al?
  - (a) They burn in oxygen to give oxides at high temperature.
  - (b) Their halides are Lewis acids.
  - (c) They combine with nitrogen to form nitrides.
  - (d) They react with HCl to form chlorides.
- 18. Unlike the other elements of its group, carbon does not form  $CX_2$  type molecules because
  - (a) energetically this is not possible
  - (b) carbon undergoes catenation
  - (c) it is non-metallic
  - (d) carbon does not contain *d*-orbital.
- 19. Which of the following statements is not correct?
  - (a) Silicon is extensively used as a semiconductor.
  - (b) Carborundum is SiC.
  - (c) Silicon occurs in free state in nature.
  - (d) Mica contains the element silicon.
- **20.** Covalency of B in  $BF_4^-$  is
  - (a) 5
- (b) 4
- (c) 3
- (d) 2

#### **SOLUTIONS**

- 1. (b): Due to larger size of Cl, AlCl<sub>3</sub> is a covalent compound (Fajan's rule).
- 2. (a)
- 3. (c): Borosilicate glass is heat resistant, because it has low coefficient of expansion.
- **(b)**
- 5. (a): HNO<sub>3</sub> is the best solvent for lead.

 $Pb + 4HNO_3(conc.) \longrightarrow Pb(NO_3)_2 + 2NO_2 + 2H_2O$ 

- **6. (b)**: Elements *Y* can probably be tin which conducts electricity and belongs to group 14. SnCl<sub>4</sub> is colourless volatile liquid whereas SnCl<sub>2</sub> is colourless solid.
- 7. (c): C forms two oxides CO and  $CO_2$ . CO is neutral and poisonous. CO<sub>2</sub> can be compressed to a refrigerant dry ice or solid CO<sub>2</sub>. SiO is unstable. SnO and PbO are amphoteric in nature.

- 8. (d): For example, PbI<sub>4</sub> does not exist because Pb<sup>4+</sup> ion is strong oxidising agent and I<sup>-</sup> ion is strong reducing agent. Thus, Pb4+ cannot exist in presence of I<sup>-</sup> ion and get reduced to Pb<sup>2+</sup> ion.
- 9. (a)
- 10. (a): Bauxite powder on heating with coke in presence of N<sub>2</sub> produces aluminium nitride which on reaction with water produces ammonia.

$$Al_2O_3 + 3C + N_2 \longrightarrow 2AlN + 3CO$$
  
Bauxite

$$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$$

- 11. (b): Bond strength of M M bond and the tendency for catenation decreases in the order C - C > Si - Si > Ge - Ge > Sn - Sn. Greater the bond energy greater is the strength of bond.
- 12. (a): Al(OH)<sub>3</sub> ppt. first formed redissolves in NaOH to form sod. meta aluminate where Al is a part of anion  $AlO_2^-$
- 13. (a): The oxidation of sodium borohydride with iodine in diglyme gives diborane.

$$2\text{NaBH}_4 + \text{I}_2 \xrightarrow{\text{Diglyme}} \text{B}_2\text{H}_6 + 2\text{NaI} + \text{H}_2$$

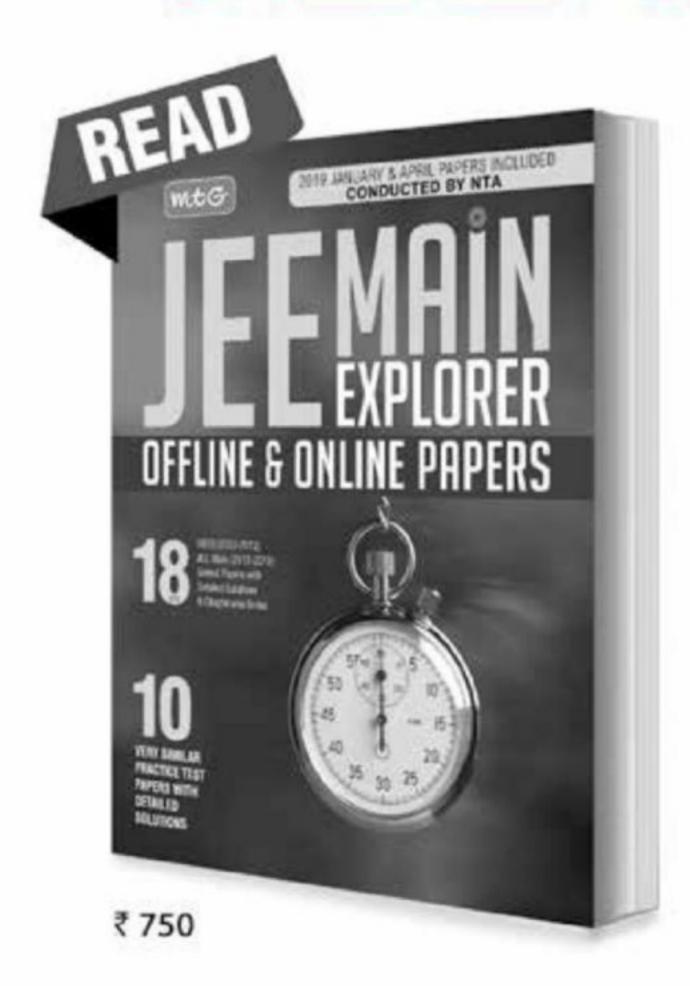
- 14. (b): Limestone and silica are the main components of cement.
- 15. (d): Ge has greater tendency to show +4 oxidation state.
- 16. (c):  $SiO_2 + 3C \xrightarrow{\Delta} SiC + 2CO$
- 17. (d): Boron being non-metal does not displace hydrogen from HCl to produce its chloride.
- 18. (a): The elements of group 14 show tetravalency by sharing four of its valence electrons. They have O.S. of +4. Ge, Sn and Pb also show +2 O.S. The stability of dihalides increases down the group. The stability of dihalides follow the sequence

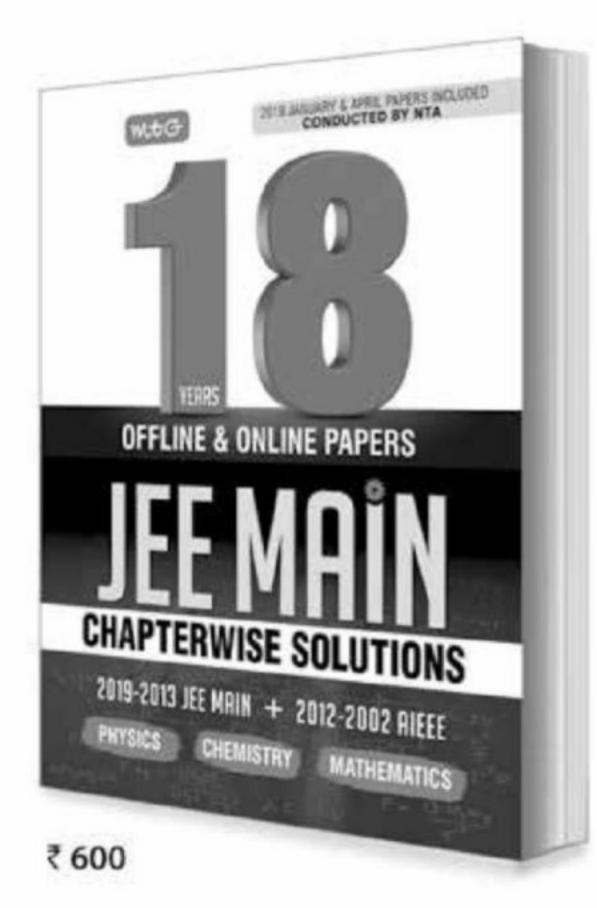
$$CX_2 \ll SiX_2 \ll GeX_2 \ll SnX_2 \ll PbX_2$$

- 19. (c): Si widely occurs as SiO<sub>2</sub>
- **20.** (b): Covalency of B in  $BF_4^-$  is 4 which is its maximum covalency also.

EXAM ALERT 2020		
Exam Date		
JEE Main I	6 <sup>th</sup> to 11 <sup>th</sup> January	
WB JEE	2 <sup>nd</sup> February	
JEE Main II	3 <sup>rd</sup> to 9 <sup>th</sup> April	
NEET	3 <sup>rd</sup> May	
JEE Advanced	17 <sup>th</sup> May	

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Series 6

The p-Block Elements

Organic Chemistry – Some Basic Principles and Techniques

Time Allowed: 3 hours Maximum Marks: 70

#### **GENERAL INSTRUCTIONS**

- (i) All questions are compulsory.
- (ii) Section A: Q.no. 1 to 20 are very short answer questions (objective type) and carry 1 mark each.
- (iii) Section B: Q.no. 21 to 27 are short answer questions and carry 2 marks each.
- (iv) Section C: Q.no. 28 to 34 are long answer questions and carry 3 marks each.
- (v) Section D: Q.no. 35 to 37 are also long answer questions and carry 5 marks each.
- (vi) There is no overall choice. However an internal choice has been provided in two questions of two marks, two questions of three marks and all the three questions of five marks weightage. You have to attempt only one of the choices in such questions.
- (vii) Use log tables if necessary, use of calculators is not allowed.

#### **SECTION-A**

#### Read the given passage and answer the questions 1 to 5 that follow:

Boron forms a number of hydrides having the general formula  $B_nH_{n+4}$  and  $B_nH_{n+6}$ . These hydrides are called boranes. The simplest hydride of boron is diborane,  $B_2H_6$ . Boranes contain special types of bonds known as multicentre bonds. Boranes have high heat of combustion.

- 1. How many 2-centered 2-electron bonds and 3-centered-2-electron bonds are there in the structure of diborane?
- 2. Complete the following reaction:  $B_2H_6 + NH_3 \xrightarrow{\text{Heat}} (NCT \ 2014)$
- 3. Draw the structure of diborane.
- 4. What happens when diborane undergoes reaction with carbon monoxide?
- 5. Give a laboratory method to prepare diborane.

#### Question 6 to 10 are one word answer:

6. Which hybrid orbital is used by underlined carbon in the following molecule?

$$CH_3-CH=\underline{C}H_2$$

- Name the metal which is commonly used as a reducing agent in metallurgical operations.
- 8. Write the IUPAC name of CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-COOH

(KVS 2017)

- Name the gas which is evolved in the Kjeldahl's method used for the estimation of nitrogen gas.
- 10. Which is the basic building unit of all silicates?

#### Questions 11 to 15 are multiple choice questions:

- 11. Which of the following statements is not correct regarding graphite and inorganic graphite?
  - (a) Both are slippery in nature.
  - (b) Both conduct electricity but graphite is less conducting in nature as compared to inorganic graphite

- (c) Graphite is not having any charge separation like inorganic graphite.
- (d) All atoms in graphite as well as in inorganic graphite are sp<sup>2</sup> hybridized.
- 12. The descending order of stability of the following carbonium ions is

$$C_6H_5\overset{+}{C}H_2$$
,  $p$ -(CH<sub>3</sub>O) $C_6H_4\overset{+}{C}H_2$ ,  $p$ -(NO<sub>2</sub>) $C_6H_4\overset{+}{C}H_2$   
(II) (III)

and 
$$p$$
-(CH<sub>3</sub>)C<sub>6</sub>H<sub>4</sub> $\overset{+}{\text{CH}}_2$ 

- (a) IV > II > I > III
- (b) II > IV > III > I
- (c) II > IV > I > III (d) IV > II > III > I
- 13. Oxalic acid reacts with concentrated H<sub>2</sub>SO<sub>4</sub> to give a mixture of two gases. When this mixture is passed through caustic potash, one of the gases is absorbed. What is the product formed by the absorbed gas with caustic potash?
  - (a)  $K_2SO_4$
- (b) KHCO<sub>3</sub>
- (c)  $K_2CO_3$
- (d) KOH

14. The reaction,  

$$C_6H_6 + Br_2 \xrightarrow{FeBr_3} C_6H_5Br + HBr$$
 is

- (a) an electrophilic addition reaction
- (b) a nucleophilic substitution reaction
- (c) an electrophilic substitution reaction
- (d) a nucleophilic addition reaction.
- 15. The substance used as an adsorbent in the column chromatography is

  - (a)  $Na_2O$  (b)  $Na_2SO_4$  (c)  $Al_2O_3$
- (d) alum.

#### Questions 16 to 20:

- (a) Both assertion and reason are correct statements, and reason is the correct explanation of the assertion.
- (b) Both assertion and reason are correct statements, but reason is not the correct explanation of the assertion.
- (c) Assertion is correct, but reason is wrong statement.
- (d) Assertion is wrong, but reason is correct statement.
- 16. Assertion: In the case of polyfunctional compounds, the choice of principal functional group is made on the basis of order of preference.

Reason: The order of decreasing priority for some functional groups is

-COOH, -COOR, -COCl, -CONH<sub>2</sub>, -CN, -CH=O, 
$$C=0$$
, -OH,  $C=C$ , -C $\equiv C-$ .

17. Assertion: Zeolites are the three-dimensional network of alumino silicates.

Reason: Negative charge on zeolite structure is neutralised by positively charged Al<sup>3+</sup> ions.

18. Assertion: Paper chromatography is a type of partition chromatography.

**Reason**: Moving phase is liquid and stationary phase is solid.

**19. Assertion**: Sn in +2 oxidation state is a reducing agent while Pb in +4 state is an oxidising agent.

**Reason**: Inert pair effect is due to participation of s-electrons in bond formation.

**20. Assertion**: The order of stability of carbocations is  $3^{\circ} > 2^{\circ} > 1^{\circ}$ .

**Reason :** Carbon atom in carbocation is in  $sp^3$  state of hybridisation.

#### **SECTION-B**

21. Suggest a reason as to why CO is poisonous.

(NCERT, KVS 2013, 2014) (HOTS)

#### OR

Complete the reactions:

- (a)  $B_2H_6 + Cl_2$  Heat
- (b)  $Na_2B_4O_7 + HCl + H_2O \longrightarrow$
- **22.** Explain why

 $CH_2 = CH^-$  is a better nucleophile than  $CH \equiv C^-$ .

- 23. What are silicones? How are they prepared?
- 24. How many metamers of 3-pentanone are possible? Write their structures and IUPAC names.

#### OR

- (a) In which C—C bond of CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Br, the inductive effect is expected to be the least?
- (b) Explain why the following two structures, I and II cannot be the major contributors to the real structure of CH<sub>3</sub>COOCH<sub>3</sub>.

- 25. Describe what happens when boric acid is heated.
- **26.** Explain the principle of paper chromatography.
- 27. Which of the following ions is more stable? Give reason.

$$(A)$$
 $\stackrel{\overset{\bullet}{C}H_2}{\longleftrightarrow}$ 
 $(B)$ 

#### **SECTION-C**

- 28. Give reasons:
  - (a) Conc. HNO<sub>3</sub> can be stored in aluminium container.
  - (b) A mixture of dilute NaOH and aluminium pieces is used to open drain.
  - (c) Aluminium alloys are used to make aircraft body.

#### OR

Give the reaction for the following:

- (i) Silicon is heated with methyl chloride at high temperature in the presence of copper.
- (ii) Silicon dioxide is treated with hydrogen fluoride.
- (iii) Hydrated alumina is treated with aqueous NaOH solution.
- Arrange the following in order of property mentioned against each.

$$\text{CH}_3$$
- $\text{CH}_2$ - $\text{CH}_2$ - $\text{CH}_2$ 
[Increasing stability]

(ii) HCOOH, CH<sub>3</sub>COOH, CH<sub>3</sub>CH<sub>2</sub>COOH [Increasing acidic strength]

[Increasing stability]

30. 0.35 g of an organic substance was Kjeldahlised and the ammonia obtained was passed into 100 mL of N/5 H<sub>2</sub>SO<sub>4</sub>. The excess acid required 154 mL of N/10 NaOH for neutralisation. Calculate the percentage of nitrogen in the compound.

#### OR

In a Dumas nitrogen estimation method,  $0.30\,\mathrm{g}$  of an organic compound gave  $50\,\mathrm{cm}^3$  of  $\mathrm{N}_2$  collected at  $300\,\mathrm{K}$  and  $715\,\mathrm{mmHg}$  pressure. Calculate the percentage composition of nitrogen in the compound. (Vapour pressure of water at  $300\,\mathrm{K}$  is  $15\,\mathrm{mmHg}$ .)

(NCERT, NCT 2008, KVS 2017)

- **31.** Starting from SiCl<sub>4</sub>, prepare the following:
  - (i) silicon
  - (ii) silica gel
  - (iii) Na<sub>2</sub>SiO<sub>3</sub>
- **32.** Identify the following types of organic reactions:
  - (a)  $CH_3CH_2Br + HS^- \longrightarrow CH_3CH_2SH + Br^-$
  - (b)  $(CH_3)_2C=CH_2 + HCl \longrightarrow (CH_3)_2ClC-CH_3$
  - (c)  $CH_3CH_2Br + HO^- \longrightarrow CH_2 = CH_2 + H_2O + Br^-$
- 33. Account for the following:
  - (a) BCl<sub>3</sub> exist as a monomer while AlCl<sub>3</sub> exist as a dimer.
  - (b) AlCl<sub>3</sub> exists but TlCl<sub>3</sub> does not.
- **34.** (i) Define hyperconjugation effect.
  - (ii) Identify the nucleophiles from the following:  $R_3N_1, > C = O_1, NC^-$

(iii) Why is hyperconjugation called no-bond resonance?

#### **SECTION-D**

- **35.** (a) Draw the resonance structures of the following compounds:
  - (i)  $CH_2 = CH \ddot{C}I$ :
  - (ii)  $CH_2 = CH CH = CH_2$
  - (iii)  $CH_2 = CH C = O$
  - (b) Identify the most stable species in the following set of ions by giving reasons:
  - (i)  $\overset{+}{C}H_3$ ,  $\overset{+}{C}H_2$ Br,  $\overset{+}{C}HBr_2$ ,  $\overset{+}{C}Br_3$
  - (ii) CH<sub>3</sub>, CH<sub>2</sub>Cl, CHCl<sub>2</sub>, CCl<sub>3</sub>

#### OR

- (a) Write the name of the isomerism shown by the following pairs:
  - (i) buta-1,3-diene and but-1-yne
  - (ii) ethoxybutane and propoxypropane
- (b) Why 3° carbocations are more stable than 1° carbocations?
- (c) Compare inductive and electromeric effects.
- (d) Why CCl<sub>3</sub>COOH is a stronger acid than (CH<sub>3</sub>)<sub>3</sub>CCOOH? (KVS 2016)
- **36.** Compound (*X*) on reduction with LiAlH<sub>4</sub> gives a hydride (*Y*) containing 21.72% hydrogen along with other products. The compound (*Y*) reacts with air explosively resulting in boron trioxide. Identify (*X*) and (*Y*). Give balanced reactions involved in the formation of (*Y*) and its reaction with air.

#### OR

Describe the general trends for the following properties of groups 13 elements.

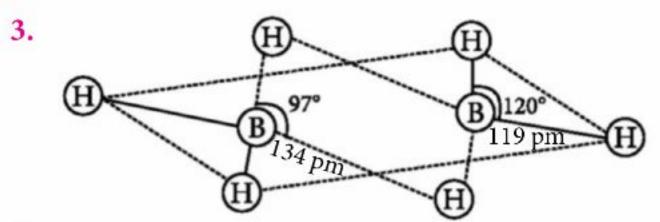
- (i) Atomic size
- (ii) Ionisation enthalpy
- (iii) Metallic character
- (iv) Oxidation states
- (v) Nature of halides.
- 37. (a) What is the difference between distillation, distillation under reduced pressure and steam distillation?
  - (b) Why is nitric acid added to sodium extract before adding silver nitrate for testing halogens?

#### OR

- (a) Draw structures of all isomeric ethers corresponding to the molecular formula  $C_5H_{12}O$ .
- (b) Give IUPAC names for the following compounds:

#### **SOLUTIONS**

- 1. The four terminal B—H bonds are regular two centred-two electron bonds while the two bridge (B—H—B) bonds are different and can be described as three centred-two electron bonds.
- 2.  $3B_2H_6 + 6NH_3 \xrightarrow{\Delta} 2B_3N_3H_6 + 12H_2$



- 4.  $B_2H_6 + 2CO \longrightarrow 2 BH_3 \cdot CO$  (Addition Compound)
- 5. A laboratory method for the preparation of diborane involves the oxidation of sodium borohydride with iodine.

$$2\text{NaBH}_4 + \text{I}_2 \xrightarrow{\text{Diglyme}} \text{B}_2\text{H}_6 + 2\text{NaI} + \text{H}_2$$

- $6. sp^2$
- 7. Aluminium
- 8. Pentanoic acid
- 9. Ammonia gas
- **10.**  $SiO_4^{4-}$
- 11. (b)
- 12. (c): Stability of carbocations is enhanced by
- (i) conjugation
- (ii) and presence of groups having +I effect.
- So, the correct order is

$$CH_2$$
 $CH_2$ 
 $CH_2$ 
 $CH_2$ 
 $CH_2$ 
 $CH_2$ 
 $CH_2$ 
 $CH_2$ 
 $CH_2$ 
 $CH_2$ 
 $CH_2$ 

13. (c): 
$$| COOH COOH COOH COO_2 + H_2OO$$

$$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$
  
Caustic potash

- 17. (c): Zeolites are the three-dimensional aluminosilicates in which few Si atoms are replaced by Al atoms. The acquired negative charge on zeolite structure is balanced by cations such as Na<sup>+</sup>, K<sup>+</sup> or Ca<sup>2+</sup>, etc.
- 18. (c)
- 19. (c): In heavier elements, the tendency to show +2 oxidation state increases in the sequence Ge < Sn < Pb. It is due to the inability of  $ns^2$  electrons of valence shell to participate in bonding (inert pair effect).
- 20. (c)
- 21. The poisonous nature of carbon monoxide (CO) is due to its ability to form a complex with haemoglobin which is about 300 times more stable than the oxygen-haemoglobin complex. This (CO-haemoglobin complex) prevents haemoglobin (in the red blood corpuscles) from carrying oxygen in the body and ultimately resulting in death.

OR

- (a)  $B_2H_6 + Cl_2 \xrightarrow{\Delta} B_2H_5Cl + HCl$
- (b)  $Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 4B(OH)_3 + 2NaCl$
- **22.** In  $H_2C=CH^-$ , the carbon atom carrying the -ve charge is  $sp^2$ -hybridized while in  $CH \equiv C^-$  the carbon atom carrying the -ve charge is sp-hybridized. Since a  $sp^2$ -hybridized carbon is less electronegative than a sp-hybridized carbon, therefore,  $H_2C=CH^-$  is a better nucleophile than  $HC \equiv C^-$ .
- 23. They are organosilicon polymers having Si O Si linkages, the main unit being  $R_2SiO$ , (where R = alkyl or aryl groups). They are called silicones as their empirical formula ( $R_2SiO$ ) resembles that of ketones ( $R_2CO$ ). Silicones are prepared by hydrolysis of alkyl or aryl substituted chlorosilanes and their subsequent polymerisation.
- 24. Two metamers (I and II) of 3-pentanone are possible:

#### OR

- (a) Magnitude of inductive effect diminishes as the number of intervening bonds increases. Hence, the effect is least in the bond between carbon-2 and carbon-3.
- (b) The two structures are less important contributors as they involve charge separation. Additionally, structure (I) contains a carbon atom with an incomplete octet.
- 25. Boric acid on heating above 370 K leads to partial removal of water to yield metaboric acid, HBO<sub>2</sub>. Further

heating yields boron sesquioxide, B<sub>2</sub>O<sub>3</sub> which is the principal oxide of boron and is considered as anhydride of boric acid.

- 26. The underlying principle of paper chromatography is that of partition chromatography which is based on continuous differential partitioning of components of mixture between stationary and mobile phases. In paper chromatography, the paper used has water trapped in it which acts as the stationary phase while a suitable solvent or a mixture of solvents is used as a mobile phase.
- **27.** Out of the following two ions, carbocation (A) is more stable than carbocation (B).

$$(A)$$
 $\stackrel{\overset{+}{C}H_2}{\longleftrightarrow} (B)$ 

The reason being that carbocation (A) is more planar and hence is stabilized by resonance. On the other hand, carbocation (B) is less planar and hence does not stabilised by resonance.

- **28.** (a) Conc. HNO<sub>3</sub> can be stored in aluminium container because conc. HNO<sub>3</sub> makes aluminium passive due to the formation of a protective layer of Al<sub>2</sub>O<sub>3</sub> on its surface.
- (b) Aluminium reacts with NaOH to give sodium tetrahydroxoaluminate (III) ion and hydrogen gas. Hydrogen gas exerts pressure on the material blocking the drain and washes it down the drain.
- (c) Aluminium alloys are used for making aircraft body because these are light in weight, corrosion resistant, strong and highly ductile.

(i)  $CH_3Cl + Si \xrightarrow{Cu \text{ powder}} CH_3SiCl_3 + (CH_3)_2SiCl_2 + CH_3SiCl_3 + (CH_3)_3SiCl + (CH_3)_4SiCl_3 + (CH_3)_4SiCl_3$ 

(ii)  $SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$ 

 $SiF_4 + 2HF \longrightarrow H_2SiF_6$ 

(iii)  $Al_2O_3$ .  $2H_2O_{(s)} + 2NaOH_{(aq)} \xrightarrow{Heat}$ Hydrated alumina  $2NaAlO_2 + 3H_2O$ Sodium

meta-aluminate

29. (i) CH<sub>3</sub> -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>

(ii) CH<sub>3</sub>CH<sub>2</sub>COOH < CH<sub>3</sub>COOH < HCOOH

**30.** Volume of N/5 H<sub>2</sub>SO<sub>4</sub> solution taken = 100 mL The volume of N/5 H<sub>2</sub>SO<sub>4</sub> neutralised by N/10 NaOH can be obtained as follows :

$$N_{
m acid} imes V_{
m acid} = N_{
m alkali} imes V_{
m alkali}$$

$$\frac{N}{5} \times V_{acid} = \frac{N}{10} \times 154 \,\text{mL}$$

$$V_{\text{acid}} = \frac{154}{10} \times 5 \,\text{mL} = 77 \,\text{mL}$$

Therefore, volume of N/5 H<sub>2</sub>SO<sub>4</sub> used for neutralising NH<sub>3</sub> = (100 - 77) mL = 23 mL Then,

% of nitrogen in the sample =

1.4×Normality of acid × Volume of acid used

for neutralising NH<sub>3</sub>

Mass of the compound taken

% of nitrogen in the sample =  $\frac{1.4 \times 1/5 \times 23}{0.35}$  = 18.4

OR

Volume of nitrogen collected at 300 K and 715 mmHg pressure is 50 mL.

Actual pressure = 715 - 15 = 700 mmHg

Volume of nitrogen at STP =  $\frac{273 \times 700 \times 50}{300 \times 760}$  = 41.9 mL

22,400 mL of  $N_2$  at STP will weighs = 28 g

41.9 mL of nitrogen will weigh =  $\frac{28 \times 41.9}{22400}$  g

% of nitrogen = 
$$\frac{28 \times 41.9 \times 100}{22400 \times 0.3} = 17.46\%$$

31. (i)  $SiCl_4 + 2Mg \longrightarrow Si + 2MgCl_2$ 

(ii) 
$$SiCl_{4(l)} + 2H_2O_{(l)} \xrightarrow{\Delta} Si(OH)_{4(aq)} \xrightarrow{\Delta} SiO_2 \cdot xH_2O_{(s)}$$
  
Silicic acid Silica gel

(iii) 
$$2\text{SiCl}_{4(g)} + 4\text{H}_2\text{O}_{(l)} \xrightarrow{\text{High temp.} \atop \text{O}_2 - \text{H}_2 \text{ flame}} 2\text{SiO}_{2(s)} + 8\text{HCl}_{(g)}$$
  
 $\text{SiO}_2 + 2\text{NaOH} \xrightarrow{\text{Fuse}} \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O}$ 

- **32.** (a) In the given reaction, "SH, a nucleophile displaces Br from the bromoalkane. Since, the reaction is brought about by a nucleophile and substitution occurs thereafter, the reaction will be termed as a nucleophilic substitution reaction.
- (b) In the given reaction, we see that the H<sup>+</sup> and Cl<sup>-</sup> reacted with the alkene and thus, produced a haloalkane. However, no atom has been displaced. Thus, the reaction is an electrophilic addition reaction.
- (c) In the given reaction, there is no atom which is displaced or substituted. Although the reaction is brought about by a nucleophile OH<sup>-</sup>, it is not a nucleophilic substitution. An HBr molecule has been removed from the reactant and hence, it is an elimination reaction.

33. (a) Due to small size of boron, there is a dative  $p\pi - p\pi$  bonding takes place between the lone pair of Cl atoms and vacant *p*-atomic orbital of B. Hence, BCl<sub>3</sub> is a monomer.

Due to large size, Al cannot participate in dative  $p\pi$ – $p\pi$  bonding. Therefore, in order to complete the octet, AlCl<sub>3</sub> dimerizes.

- (b) Because as we move down the group, the tendency of  $ns^2$  electron to remain inert increases (inert pair effect). Therefore, only one electron from the p-atomic orbital participates in the bond formation and hence +1 oxidation state becomes more and more stable as compared to +3 oxidation state. Therefore, Tl forms only TlCl.
- **34.** (i) When an alkyl group is attached to an unsaturated system such as a double bond or a benzene ring, the order of inductive effect is actually reversed. This effect is called hyperconjugation effect or Baker-Nathan effect.

(ii) NC

(iii) Hyperconjugation is called no-bond resonance because the hydrogen bonded to carbon looses its bond from carbon during resonance.

35. (a) (i) 
$$\overrightarrow{CH_2} = \overrightarrow{CH} + \overrightarrow{C} : \overrightarrow{CH_2} - \overrightarrow{CH} = \overset{+}{C} : \overrightarrow{CH_2} - \overset{+}{$$

(ii) 
$$CH_2 = CH - CH = CH_2 \longleftrightarrow$$
  
 $\dot{C}H_2 - CH = CH - \ddot{C}H_2 \longleftrightarrow$   
 $\ddot{C}H_2 - CH = CH - \dot{C}H_2$   
 $\ddot{C}H_2 - CH = CH - \dot{C}H_2$ 

$$(iii)CH2 = CH - CH + CH2 - CH = C-H$$

- (b) (i)  $\overset{\neg}{C}H_3$  is most stable because the replacement of hydrogen by bromine increases positive charge on carbon atom and destabilises the species.
- (ii)  $\bar{C}Cl_3$  is most stable because electronegativity of chlorine is more than hydrogen. Negative charge on carbon is reduced which results in more stability.

OR

(a) (i) Functional isomerism: H<sub>2</sub>C=CH−CH=CH<sub>2</sub> and HC≡C−CH<sub>2</sub>CH<sub>3</sub> Buta-1, 3 diene But-1-yne

(ii) Metamerism:

- (b) Hyperconjugation interaction in  $(CH_3)_3\overset{+}{C}$  is greater than in  $CH_3\overset{+}{C}H_2$  as  $(CH_3)_3\overset{+}{C}$  has nine C-H bonds.
- (c) Inductive effect is a permanent effect caused due to more or less electronegative atom/group attached to carbon in an organic compound.

$$-\overset{\delta\delta\delta^{+}}{C}\overset{\delta\delta^{+}}{\longrightarrow}\overset{\delta^{+}}{C}\overset{\delta^{-}}{\longrightarrow}X$$

Electromeric is a temporary electron displacement caused in carbon chain due to presence of an external electrophile or nucleophile.

(d) CCl<sub>3</sub>COOH is a stronger acid than (CH<sub>3</sub>)<sub>3</sub>CCOOH due to presence of three electron withdrawing groups (*I*-effect). This reduces electron density of —OH bond and hence, make it more acidic.

36. 
$$X \xrightarrow{\text{LiAlH}_4} (Y)$$

 $Y + air \longrightarrow B_2O_3$ 

From this we can guess 'Y' must be  $B_2H_6$ .

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O + Heat$$
(Y)

% of hydrogen in  $B_2H_6 = \frac{6}{27.62} \times 100 = 21.72\%$ 

[Mol. wt. of 
$$B_2H_6 = 21.62 + 6 = 27.62$$
]

Thus, percentage of hydrogen is 21.72 in  $B_2H_6$ . From this we can guess that X is boron trihalide.

$$4BX_3 + 3LiAlH_4 \rightarrow 2B_2H_6 + 3LiX + 3AlX_3 [X = Cl \text{ or Br}]$$
(X)

OR

- (i) Atomic size: Atomic radii of group-13 elements increase down the group with the exception that atomic radius of Ga is less than that of Al due to the presence of *d*-electrons which offer poor screening effect for the outer electrons from the increased nuclear charge in Ga.

  (ii) Ionisation enthalpy: For group-13 elements, the trend of ionisation enthalpy is B > Al < Ga > In < Tl. This is due to increase in size and low screening effect
- of *d* and *f* electrons.

  (iii) Metallic character: Metallic character increases from boron to aluminium then decreases down the group.
- (iv) Oxidation states: For group-13 elements, both +1 and +3 oxidation states are observed. The +1 oxidation state becomes more stable as we move down the group due to inert pair effect. Boron does not show +3 oxidation state.
- (v) Nature of halides: Group-13 elements form trihalides (except TlI<sub>3</sub>). Due to electron deficient nature, BCl<sub>3</sub> accepts electrons and forms adducts. AlCl<sub>3</sub> achieves stability by forming a dimer.

37. (a) Differences between distillation, distillation under reduced pressure and steam distillation :

Criterion for difference	Distillation	Distillation under reduced pressure	Steam distillation
Principle	It is used to separate  - volatile liquids from non-volatile impurities.  - liquids having sufficient difference in their boiling points.	It is used to purify liquids  - having very high boiling points.  - which decompose at or below their boiling point	This method is used to separate substances which are steam volatile, immiscible with water, possess a vapour pressure of 10–15 mm Hg and contain non-volatile impurities
Used for		Separation of liquids having very high boiling points or those, which decompose at or below their boiling points.	immiscible in water but are
Example	A mixture of chloroform (b.pt. 334 K) and aniline (b.pt. 457 K).	Separation of glycerol from spent  – lye in soap industry.	Separation of aniline from aniline-water mixture.

(b) If N or S is present in the compound, the sodium fusion extract is first boiled with concentrated nitric acid to decompose cyanide or sulphide of sodium during Lassaigne's test. These ions would otherwise interfere with silver nitrate test for halogens.

#### OR

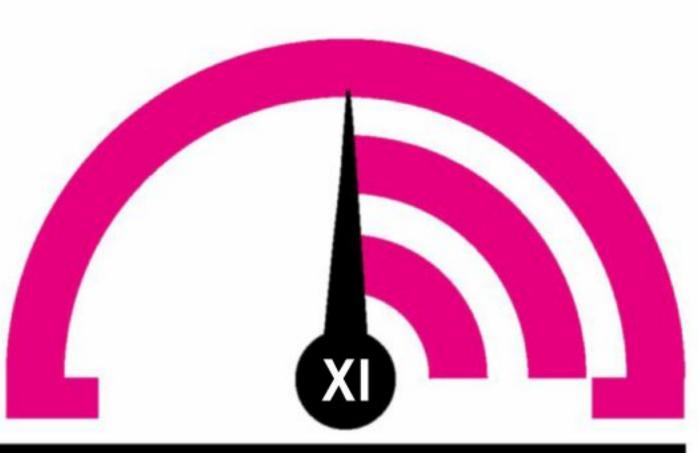
(a) The possible isomeric ethers corresponding to C<sub>5</sub>H<sub>12</sub>O are,

(i)	$C_2H_5-O-C_3H_7$	H H H H 
(ii)	$CH_3 - O - C_4H_9$	Й Н Н Н Н Н Н Н Н Н Н Н Н Н Н Н Н Н Н Н
(iii)	$CH_3CH_2 - O - CH(CH_3)_2$	H H H H H H  H H H H H  H H H H H  H H H H  H H H H  H H H H  H H H H  H H H H  H H H H
(iv)	$CH_3$ $CH_3$ $CH_3$ $CH_3$ $CH_3$	H H—C—H H—C—O—C—————————————————————————

(b) (i) Cyclohexane-1, 2-diol

(ii) 6-Chloro-2-methylhexan-3-one

## MONTHLY TEST DO RIVER TO RESERVE TO THE RESERVE TO



This specially designed column enables students to self analyse their extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

**Total Marks: 120** 

#### Some Basic Concepts of Chemistry | Structure of Atom

Time Taken: 60 Min.

#### **NEET / AIIMS**

#### **Only One Option Correct Type**

- 1. A solution of KCl has a density of 1.69 g mL<sup>-1</sup> and is 67% by weight. Find the density (g mL<sup>-1</sup>) of the solution if it is diluted so that the percentage by weight of KCl in the diluted solution is 30%.
  - (a) 1.224
- (b) 2.22
- (c) 5.68
- (d) 4.52
- 2. An electron in H atom jumps from the third energy level to the first energy level. The change in the potential energy of the electron is
  - (a) 12.09 eV
- (b) 6.04 eV
- (c) 24.18 eV
- (d) 9.24 eV
- 3. When 3.2 g S is vaporized at 450°C and 723 mm pressure, the vapours occupy a volume of 780 mL. If the molecular formula of S vapour under these conditions is S<sub>x</sub>, then the value of x is
  - (a) 6

(b) 4

(c) 2

- (d) 8
- 4. An electron beam can undergo diffraction by crystals. Through what potential should a beam of electrons be accelerated so that its wavelength becomes equal to 1.54 Å?
  - (a) 5.6 V
- (b) 24.5 V
- (c) 42.4 V
- (d) 63.4 V
- 5. An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 mL. The volume of 0.1 N NaOH required to completely neutralise 10 mL of this solution is
  - (a) 40 mL
- (b) 20 mL
- (c) 10 mL
- (d) 4 mL.

- 6. The kinetic energy of an electron in the second Bohr orbit of a hydrogen atom is
  - (a)  $\frac{h^2}{4\pi^2 m a_0^2}$
- (b)  $\frac{h^2}{16\pi^2 m a_0^2}$
- (c)  $\frac{h^2}{32\pi^2 m a_0^2}$
- (d)  $\frac{h^2}{64\pi^2 m a_0^2}$
- 7. When 10 mL of ethyl alcohol (density = 0.7893 g mL<sup>-1</sup>) is mixed with 20 mL of water (density 0.9971 g mL<sup>-1</sup>) at 25°C, the final solution has a density of 0.9571 g mL<sup>-1</sup>. The percentage change in total volume on mixing is
  - (a) 3.1%
- (b) 2.4%
- (c) 1%
- (d) none of these.
- 8. The given electronic configuration deviates from
  - ns np
  - (I) Hund's rule
  - (II) Aufbau principle
  - (III) Pauli's principle
  - (a) All of the above
- (b) Only I, II
- (c) Only I, III
- (d) Only II, III
- 9. Sulphuric acid reacts with sodium hydroxide as follows:

 $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$ 

When 1 L of 0.1 M sulphuric acid solution is allowed to react with 1 L of 0.1 M sodium hydroxide solution then the amount of sodium sulphate formed and its molarity in the solution obtained is

- (a)  $7.10 \text{ g and } 0.1 \text{ mol L}^{-1}$
- (b) 7.10 g and  $0.025 \text{ mol L}^{-1}$
- (c) 5.40 g and  $0.1 \text{ mol L}^{-1}$
- (d) 3.55 g and  $0.025 \text{ mol L}^{-1}$ .
- 10. When electronic transition occurs from higher energy state to lower energy state with energy difference equal to  $\Delta E$  electron volts, the wavelength of the line emitted is approximately equal to  $(h = 6.62 \times 10^{-34} \text{ Js})$ 

  - (a)  $\frac{12397}{\Delta E} \times 10^{-10} \text{ m}$  (b)  $\frac{12397}{\Delta E} \times 10^{10} \text{ m}$
  - (c)  $\frac{12397}{\Lambda E} \times 10^{-10}$  cm (d)  $\frac{12397}{\Lambda E} \times 10^{10}$  cm
- 11. Two oxides of a certain metal were separately heated in a current of hydrogen until constant weights were obtained. The water produced in each case was carefully collected and weighed. 2 g of each oxide gave, respectively 0.2517 g and 0.4526 g of water. This observation illustrates
  - (a) law of conservation of mass
  - (b) law of constant proportions
  - (c) law of multiple proportions
  - (d) law of reciprocal proportions.
- 12. The decreasing order of energy for an electrons represented by the following sets of quantum number is
  - 1. n = 4, l = 0, m = 0,  $s = \pm 1/2$
  - 2. n = 3, l = 1, m = 1, s = -1/2
  - 3. n = 3, l = 2, m = 0, s = +1/2
  - 4. n = 3, l = 0, m = 0, s = -1/2
  - (a) 1 > 2 > 3 > 4
- (b) 2 > 1 > 3 > 4
- (c) 3 > 1 > 2 > 4 (d) 4 > 3 > 2 > 1

#### Assertion & Reason Type

**Directions**: In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as:

- If both assertion and reason are true and reason is the correct explanation of assertion.
- If both assertion and reason are true but reason is not the correct explanation of assertion.
- If assertion is true but reason is false.
- If both assertion and reason are false.
- 13. Assertion: If 100 mL of 0.2 N HCl is mixed with 100 mL of 0.3 N HCl, the normality of final solution will be 0.25 N.

Reason: If two solutions of the same solute are mixed, the normalities can be added.

- **14. Assertion**: Orbitals with the same value of l and  $m_l$ have the same angular wave function.
  - Reason: Angular wave function doesn't depend upon the *n*.
- 15. Assertion: For a solution, 92 g of ethanol and 144 g of water is mixed, mole fraction of ethanol and water in the solution is 0.2 and 0.8 respectively.

**Reason:** The sum of the mole fractions of all the components in a solution is unity.

#### **JEE MAIN / ADVANCED**

#### Only One Option Correct Type

- 16. Photoelectric emission is observed from a surface for frequencies  $v_1$  and  $v_2$  of the incident radiation  $(v_1 > v_2)$ . If the maximum kinetic energies of the photo-electrons in the two cases are in the ratio 1:kthen the threshold frequency  $v_0$  is given by
  - (a)  $\frac{v_2 v_1}{k 1}$
- (b)  $\frac{kv_1 v_2}{k 1}$
- (c)  $\frac{kv_2 v_1}{k-1}$  (d)  $\frac{v_2 v_1}{k}$
- 17. 1.2 g mixture of Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> was dissolved in water to form 100 cm<sup>3</sup> of a solution. 20 cm<sup>3</sup> of this solution required 40 cm3 of 0.1 N HCl for neutralisation. What will be the weight of Na<sub>2</sub>CO<sub>3</sub> and  $K_2CO_3$  in the mixture?
  - (a)  $Na_2CO_3 = 0.596$  g,  $K_2CO_3 = 0.604$  g
  - (b)  $Na_2CO_3 = 1.56 \text{ g}$ ,  $K_2CO_3 = 2.46 \text{ g}$
  - (c)  $Na_2CO_3 = 3.52 \text{ g}$ ,  $K_2CO_3 = 5.6 \text{ g}$
  - (d)  $Na_2CO_3 = 4.56 \text{ g}$ ,  $K_2CO_3 = 0.24 \text{ g}$
- 18. The atomic spectrum of hydrogen is found to contain a series of lines at wavelengths (in nm) 656.46, 486.27, 434.17 and 410.29. What will be the wavelength of the next line in the series?
  - (a) 2.56 nm
- (b) 6.52 nm
- (c) 1.592 nm
- (d) 397·1 nm
- 19. The mass of one litre sample of ozonised oxygen at N.T.P. was found to be 1.5 g. When 100 mL of this mixture at N.T.P. were treated with turpentine oil, the volume was reduced to 90 mL. The molecular mass of ozone is
  - (a) 98
    - (b) 48
- (c) 56
- (d) 68

#### More than One Options Correct Type

- 20. Choose the correct statement(s) regarding the photoelectric effect.
  - (a) No electrons are ejected, regardless of the intensity of the radiation, unless the frequency

- exceeds a threshold value characteristic of the metal.
- (b) The kinetic energy of the ejected electrons varies linearly with frequency of the incident radiation and its intensity.
- (c) Even at low intensities, electrons are ejected immediately if the frequency is above the threshold value.
- (d) An intense and weak beam of monochromatic radiations differ in having number of photons and not in the energy of photons.
- 21. Which of the following statements are correct?
  - (a) A sample of  $CaCO_3$  contains Ca = 40%, C = 12%, and O = 48%. If the law of constant composition is true, then the mass of Ca in 10 g of CaCO<sub>3</sub> from another source is 4.0 g.
  - (b) 12 g of carbon is heated in vacuum and there is no change in the mass, is the best example of the law of conservation of mass.
  - (c) Air is heated at constant pressure and there is no change in mass but the volume increases, is the best example of the law of conservation of mass.

- (d) SO<sub>2</sub> gas was prepared by (i) heating Cu with conc. H<sub>2</sub>SO<sub>4</sub>, (ii) burning sulphur in oxygen, (iii) reacting sodium sulphite (Na<sub>2</sub>SO<sub>3</sub>) with dilute  $H_2SO_4$ . It was observed that in each case, S and O combine in the ratio of 1:1. This data illustrates the law of constant composition.
- **22.** Which of the following statements are correct?
  - (a) Energy of an orbital is determined by principal quantum number.
  - (b) For all values of n, the p-orbital have the same shape, but overall size increases as *n* increases, for a given atom.
  - (c) A  $2p_x$  atomic orbital consists of two lobes of electron density.
  - (d) Magnetic quantum number =  $\sqrt{n(n+2)}$  B.M.
- 23. 1.24 g of  $P_4$  reacts with 8.0 g of  $O_2$ .

The following reactions occur:

(i) 
$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$

(ii) 
$$P_4 + 3O_2 \longrightarrow P_4O_6$$

Which of the following statements are wrong?

- (a)  $P_4$  is the limiting quantity.
- (b)  $O_2$  is the limiting quantity.
- (c) Mass of P<sub>4</sub>O<sub>10</sub> obtained is 2.2 g.
- (d) Mass of P<sub>4</sub>O<sub>6</sub> obtained is 2.84 g.

#### Scientist who Made Us Proud

Subramania Ranganathan (1934-2016), popularly known as Ranga, was an Indian bioorganic chemist and a professor and head of the department of chemistry at the Indian Institute of Technology, Kanpur. He was known for his studies on synthetic and mechanistic organic chemistry and was an elected fellow Indian National Science Academy, National Academy of Sciences, India and the Indian Academy of Sciences.



Subramania Ranganathan (2 Feb 1934 - 8 Jan 2016)

#### **Biography**

Ranganathan, born on 2 February 1934 in the south Indian state of Tamil Nadu, graduated in chemistry from Madras University and continued there to complete his master's degree. In the US, he enrolled at Ohio State University at Harold Shechter's laboratory and secured a PhD in 1962. He moved to the laboratory of Robert Burns Woodward, the 1965 Nobel laureate, at Harvard University for his post- doctoral studies and in 1964, he shifted to Woodward Research Institute, Basel to complete the studies in 1964. In 1966, he joined IIT Kanpur where he spent his entire official academic career, holding positions of a professor, head of the department and dean, before superannuating in

1994. Post-retirement, he served as an INSA senior scientist, first at National Institute for Interdisciplinary Science and Technology and later at the Indian Institute of Chemical Technology (IICT).

Ranganathan was holding the position of an honorary position at IICT when he died on 8 January 2016, at the age of 81.

During his post-doctoral days, Ranganathan worked closely with Woodward and was known to have assisted the latter in his work on Woodward-Hoffmann rules.

#### **Awards and Honors**

- Ranganathan received the Basudev Banerjee Medal in 1975 and the Council of Scientific and Industrial Research awarded him the Shanti Swarup Bhatnagar Prize in 1977.
- He received R. C. Mehrotra Endowment Gold Medal in 2000 and the Silver Medal of the Chemical Research Society of India in 2001.
- CRSI honored him again in 2006 with the Lifetime Achievement Award.
- In 2014, he was awarded the Best Teacher Award by the Indian National Science Academy.
- The Indian Academy of Sciences elected him as a fellow in 1975 and he became an elected fellow of the Indian National Science Academy and the National Academy of Sciences, India in 1981 and 1991 respectively.

#### **Numerical Value Type**

- 24. A mixture of formic acid and oxalic acid is heated with conc. H<sub>2</sub>SO<sub>4</sub>. The gas produced is collected and on its treatment with KOH solution, the volume of the gas decreased by 1/6<sup>th</sup>. If the molar ratio of the two acids in the original mixture is x : 1, then find the value of x.
- 25. If the position of the electron is measured within an accuracy of  $\pm 0.002$  nm, the uncertainty in the momentum of the electron is  $x \times 10^{-23}$  kg ms<sup>-1</sup>, then the value of x is
- 26. A 100% pure sample of a divalent metal carbonate weighing 2 g on complete thermal decomposition releases 448 cc of carbon dioxide at STP. The equivalent mass of the metal is

#### Matrix Match Type

Answer the following questions (27 and 28) by appropriately matching the columns based on the information given in the passage:

The set of an electron is described by a set of four quantum numbers.

- (i) Principal quantum number (n) gives the size of the shell and the relative average distance of an electron from the nucleus and thereby the energy of the electron.
- (ii) Azimuthal quantum number or subsidiary quantum number (l) gives the subshell and shape of the orbital for an electron. Each orbital of a given shell is degenerate. l = 0, 1, 2, 3, 4... indicates the subshell s, p, d, f, g...... respectively. A subshell is only possible when l < n and total subshells in a shell is equal to numerical value of n.
- (iii) Magnetic quantum number (m) determines the preferred orientations of orbitals in space.  $m = -l, \ldots, 0, \ldots, +l.$
- (iv) Spin quantum number (s) represents the spin of an electron. In an orbital there are maximum of two electrons such that their spins are +1/2 and -1/2and the sum of the spins is zero.

Column-I		Column-II	
P.	$n = 2, l = 1, m = \pm 1$	I.	$3d_{x^2-y^2}$ or $3d_{xy}$
Q.	n=4, l=2, m=0	II.	$2p_x$ or $2p_y$
R.	n = 4, l = 0, m = 0	III.	4s
S.	$n = 3, l = 2, m = \pm 2$	IV.	$4d_z^2$

- 27. Which of the following has the correct combination considering column I and column II?
  - (a)  $P \rightarrow II$
- (b)  $Q \rightarrow III$
- (c)  $R \rightarrow I$
- (d)  $S \rightarrow IV$
- 28. Which of the following has correct combination considering column I and column II?

(a) 
$$P \rightarrow IV(b)$$
  $Q \rightarrow I$  (c)  $R \rightarrow III(d)$   $S \rightarrow II$ 

Answer the following questions (29 and 30) by appropriately matching the columns based on the information given in the passage:

In a balanced chemical reaction the reactant which is present in the lesser amount gets consumed after sometime and after that no further reaction takes place whatever be the amount of the other reactants present. Hence, the reactant which gets consumed, limits the amount of product formed and is, therefore, called the limiting reagent.

	Column-I		Column-II	
P.	$2H_2 + O_2 \rightarrow 2H_2O$ 1.0 g 1.0 g ?	I.	0.56 g	
Q.	$N_2 + 3H_2 \rightarrow 2NH_3$ 1.0 g 1.0 g ?	II.	1.333 g	
R.	$CaCO_3 \rightarrow CaO + CO_2$ 1.0 g ?	III.	1.125 g	
S.	$C + 2H_2 \rightarrow CH_4$ 1.0 g 1.0 g ?	IV.	1.214 g	

- 29. Which of the following has correct combination considering column I and column II?
  - (a)  $P \rightarrow III(b)$   $Q \rightarrow I$  (c)  $R \rightarrow II$  (d)  $S \rightarrow IV$
- 30. Which of the following has correct combination considering column I and column II?
  - (a)  $P \rightarrow II$
- (b)  $Q \rightarrow III$
- (c)  $R \rightarrow I$
- (d)  $S \rightarrow IV$



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#### **CHECK YOUR PERFORMANCE**

.....

.....

No. of questions attempted

No. of questions correct ..... Marks scored in percentage

If your score is

> 80% 60-80% <60%

Your preparation is going good, keep it up to get high score.

Need more practice, try hard to score more next time.

Stress more on concepts and revise thoroughly.

# Class

with exclusive and brain storming MCQs

Practicing these MCQs help to strengthen your concepts and give you extra edge in your JEE preparation

### **Only One Option Correct Type**

- Which of the following is true for the species having  $3d^4$  configuration?
  - (a) Cr<sup>2+</sup> is reducing in nature.
  - (b) Mn<sup>3+</sup> is oxidising in nature.
  - (c) Both (a) and (b).
  - (d) None of these.
- The products (A) and (B) are respectively

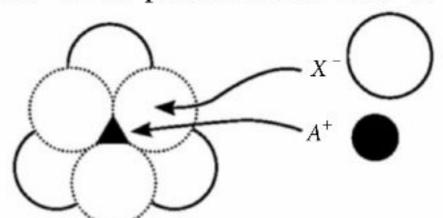
- Which of the following statements is correct regarding enzymes?
  - (a) Enzymes are specific biological catalysts that can normally function at very high temperatures ( $T \sim 1000 \text{ K}$ ).
  - (b) Enzymes are normally heterogeneous catalysts that are very specific in action.
  - (c) Enzymes are specific biological catalysts that cannot be poisoned.
  - (d) Enzymes are specific biological catalysts that possess well defined active sites.
- An element X of atomic mass 25.0 exists as  $X_4$ in benzene to the extent of 100%. When 10.30 g of saturated solution of X in benzene is added to 20⋅0 g of benzene, the depression in freezing point of the resulting solution is 0.51 K. If  $K_f$  for benzene is  $5.1 \text{ K kg mol}^{-1}$ , the solubility of X in 100 g of benzene will be
  - (a)  $3.0 \, g$
- (b)  $2.7 \, \text{g}$
- (c) 0.30 g
- (d) 0.27 g.

**5.** Compare the properties of two isomeric products *X* and *Y* formed in the following reaction :

ŌН	
	(t) CCL - KOILA
[O]	$(i) CCl_4 + KOH/\Delta \rightarrow X(Major) + Y(Minor)$
	(ii) H <sup>+</sup>

Acid strength	H <sub>2</sub> O solubility	Volatility	Melting point
(a) $Y > X$	Y > X	X > Y	Y > X
(b) $X > Y$	X > Y	Y > X	X > Y
(c) $Y > X$	X > Y	Y > X	Y > X
(d) $X > Y$	Y > X	X > Y	Y > X

6. The arrangement of  $X^-$  ions around  $A^+$  ion in solid AX is given in the figure (not drawn to scale). If the radius of  $X^-$  is 250 pm, the radius of  $A^+$  is



- (a) 104 pm
- (b) 125 pm
- (c) 183 pm
- (d) 57 pm.
- 7. Identify the products.

 $Na_2SO_3 + Cl_2 + H_2O \rightarrow Products$ 

- (a) Na<sub>2</sub>SO<sub>4</sub>, HCl
- (b) Na<sub>2</sub>S, HCl
- (c) NaClO<sub>3</sub>, S
- (d)  $Na_2S_2O_3$ , HCl
- **8.** Which of the following complexes having tetrahedral geometry?
  - (I) Ni(CO)<sub>4</sub>
  - (II) K[AgF<sub>4</sub>]
  - (III)  $Na_2[Zn(CN)_4]$
  - $(IV)K_2[PtCl_4]$
  - (V) [RhCl(PPh<sub>3</sub>)<sub>3</sub>]
  - (a) Only II, III and V
- (b) Only I, II and III
- (c) Only I, III and IV
- (d) Only I and III
- 9. Which one of the following is a chain growth polymer?
  - (a) Polymethyl methacrylate
  - (b) Nucleic acid
  - (c) Polystyrene
  - (d) Protein
- 10. Match column-I (metal) with column-II (procedure of extraction) and select the correct answer by choosing an appropriate option.

Column-I			Column-II
A.	Pb	p.	Hydrometallurgical process
B.	Cu	q.	Carbon reduction method
C.	Fe	r.	Thermite process
D.	Cr	s.	Self-reduction method

- (a)  $A \rightarrow q, s; B \rightarrow r, s; C \rightarrow q; D \rightarrow r$
- (b)  $A \rightarrow q, s; B \rightarrow p, q, r; C \rightarrow p, q; D \rightarrow p, r$
- (c)  $A \rightarrow p$ ,  $s; B \rightarrow p, q, r, s; C \rightarrow p, q, s; D \rightarrow p, q, r, s$
- (d)  $A \rightarrow p; B \rightarrow q, r; C \rightarrow r; D \rightarrow s$

### **More Than One Options Correct Type**

11. Which of the following statement are true regarding the product formed in the given reaction?

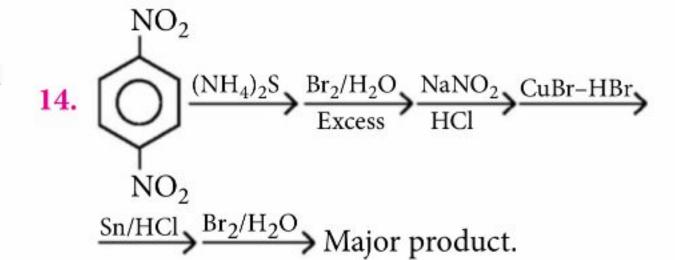
$$CH_3-CH_2-CH_2-CH_2-CH_3 \xrightarrow[CH_3]{80\% EtOH}$$

$$CH_3$$

- (a) Major product is given by S<sub>N</sub>1 reaction.
- (b) Through E1 mechanism three alkenes are formed.
- (c) 3-Methylpentan-3-ol is also formed as one of the product.
- (d) Fractional distillation of elimination product will give two fractions.
- 12. Which of the following statements are not correct for lyophilic colloids?
  - (a) These are prepared by special indirect methods.
  - (b) These are not much hydrated.
  - (c) These are also called intrinsic colloids.
  - (d) Small quantity of electrolyte is sufficient to cause precipitation of these colloids.

### **Numerical Value Type**

13. If the standard reduction potential for  $Cu^{2+}|Cu$  is +0.34 V, then the reduction potential at pH = 14 for the above couple is -xV. The value of x is  $(K_{sp} \text{ of } Cu(OH)_2 \text{ is } 1.0 \times 10^{-19})$ 



The total number of halogen atoms present in the major product is

15. The rate of a first-order reaction is 0.04 mol litre<sup>-1</sup>s<sup>-1</sup> at 10 minutes and 0.03 mol litre<sup>-1</sup> s<sup>-1</sup> at 20 minutes

after initiation. The half-life (in min) of the reaction is

### **SOLUTIONS**

1. (c):  $Cr^{2+}$  is reducing as its configuration changes from  $d^4$  to  $d^3$ , this  $d^3$  configuration can be written as  $t_{2g}^3$ , which is a more stable configuration. On the other hand, the change from  $Mn^{3+}$  to  $Mn^{2+}$  results in the half-filled ( $d^5$ ) configuration which has extra stability.

2. (a): 
$$OH \longrightarrow OH \longrightarrow OH \longrightarrow OH \longrightarrow CH_2OH \longrightarrow$$

- 3. (d)
- **4.** (a): Suppose saturated solution of X in benzene contains w g of X (present as  $X_4$ ). Hence, amount of benzene present = (10.30 w) g.

:. Total amount of benzene present

$$= 20 + (10.30 - w)g = (30.30 - w)g$$

$$\Delta T_f = \frac{1000 \times K_f \times w_2}{w_1 \times M_2}$$

$$0.51 = \frac{1000 \times 5.1 \times w}{(30.30 - w) \times 100} \ (M_2 \text{ of } X_4 = 25 \times 4 = 100)$$

or 
$$51(30.30 - w) = 5100 w$$

or 
$$30.30 - w = 100 w$$

OH

or 101 
$$w = 30.30$$
 or  $w = 0.3$  g

Thus, 10.30 g of saturated solution contains 0.3 g of X and 10 g of benzene.

 $\therefore$  Solubility of *X* in 100 g of benzene = 3.0 g

5. (d): 
$$(i) CCl_4 + KOH/\Delta \rightarrow (ii) H^+$$

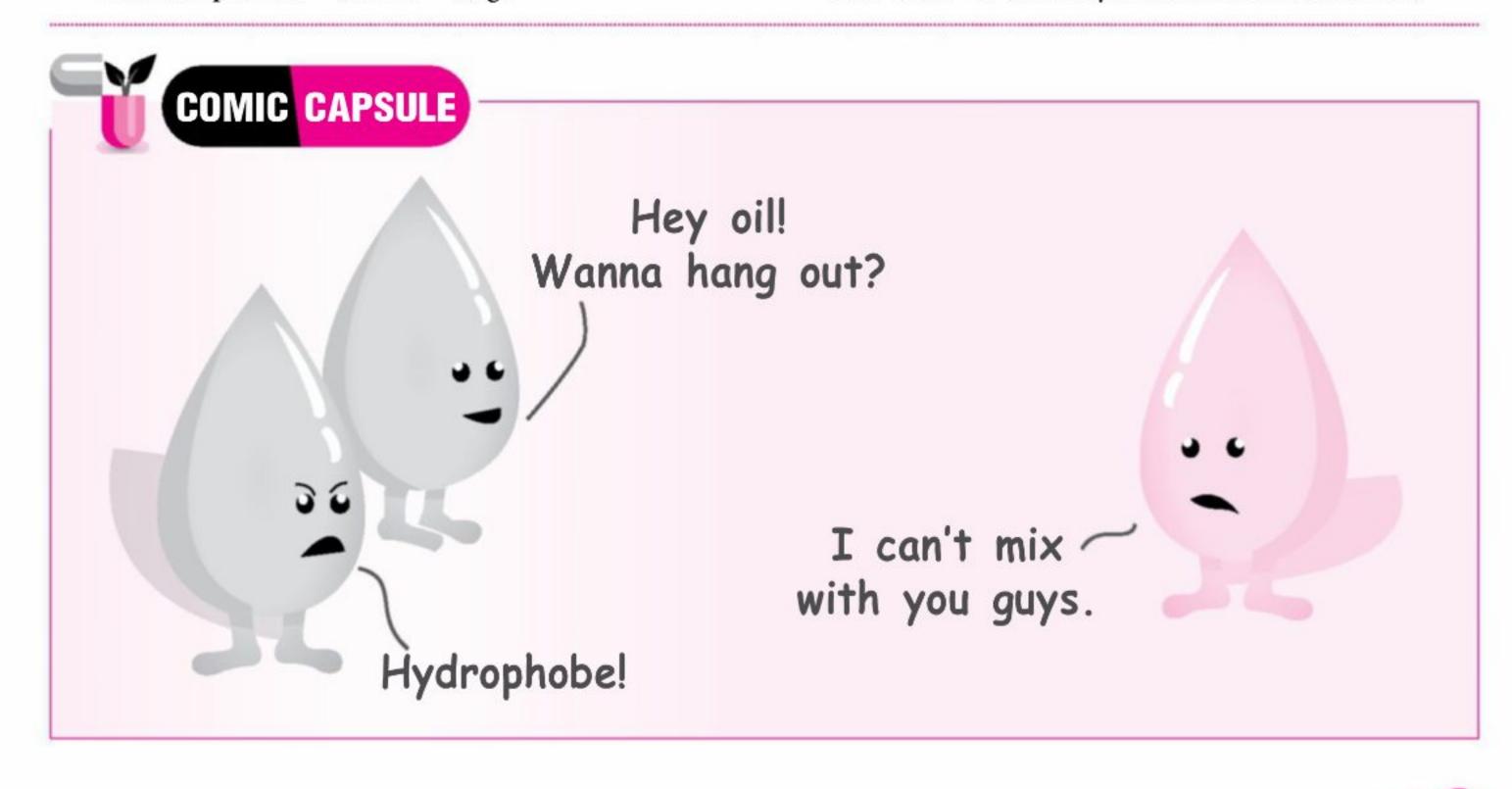
$$OH \rightarrow COOH$$

OH COOH 
$$+$$
 COOH  $(pK_a = 2.98)$  COOH  $(pK_a = 4.58)$ 

Acid strength : X > Y (Carboxylate anion stabilized by H-bonding)

Solubility in  $H_2O: Y > X$  (Intermolecular H-bonding in Y)

Volatility : X > Y (Intramolecular H-bonding in X) M.Pt. : Y > X (More symmetrical structure of Y)



6. (a) : Cation 
$$A^+$$
 occupies octahedral void arrangement by anion  $X^-$ .

$$\frac{r_{A^{+}}}{r_{X^{-}}} = 0.414$$
 $\frac{r_{A^{+}}}{250} = 0.414$  [: Radius of  $X^{-}$  ( $r_{X}^{-}$ )= 250 pm]
 $r_{A}^{+} = 0.414 \times 250 = 103.5 \approx 104$  pm

7. (a): 
$$Na_2SO_3 + Cl_2 + H_2O \rightleftharpoons Na_2SO_4 + 2HCl$$

**8.** (d):(I) It is tetrahedral 
$$(sp^3)$$
 because there is no  $(n-1)d$  orbital vacant for  $dsp^2$  hybridisation.

(II) Ag with +3 oxidation state and  $4d^8$  configuration has square planar geometry.

(III) It is tetrahedral  $(sp^3)$  because there is no (n-1)dorbital vacant for  $dsp^2$  hybridisation.

(IV) Pt with +2 oxidation state and  $5d^8$  configuration has square planar geometry.

(V) Rh with +1 oxidation state and  $4d^8$  configuration has square planar geometry.

(I) and (III) have tetrahedral geometry.

### 10. (a)

11. (a,b,c): 
$$CH_3 - CH_2 - CC - CH_2 - CH_3 = \frac{80\% \text{ EtOH}}{20\% H_2O}$$
OEt
$$CH_3 - CH_2 - CC - CH_2 - CH_3 + OH$$

$$CH_3 - CH_2 - CC - CH_2 - CH_3 + OH$$

$$CH_3 - CH_2 - CC - CH_2 - CH_3$$

$$CH_3 - CH_2 - CC - CH_2 - CH_3$$

$$CH_3 - CH_2 - CC - CH_2 - CH_3$$

$$CH_3 - CH_2 - CC - CH_2 - CH_3$$

$$CH_3 - CH_2 - CC - CH_2 - CH_3$$

$$CH_3 - CH_2 - CC - CH_2 - CH_3$$

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$$CH_3 - CH_2 - CC - CH_2 - CH_3$$

$$CH_3 - CH_2 - CC - CH_2 - CH_3$$

$$CH_3 - CH_2 - CC - CH_2 - CH_3$$

$$CH_3 - CH_2 - CC - CH_2 - CH_3$$

$$CH_3 - CH_2 - CH_3 - CH_2 - CH_3$$

$$CH_3 - CH_2 - CH_3 - CH_3$$

$$CH_3 - CH_2$$

12. (a, b, d)

13. (0.22): At pH = 14, 
$$[H^+] = 1 \times 10^{-14} \text{ M}$$
;  
 $[OH^-] = 10^0 = 1 \text{ M}$   
 $\therefore [H^+][OH^-] = 1 \times 10^{-14}$ 

 $Cu(OH)_2$  ionises as follows:

Cu(OH)<sub>2</sub> 
$$\Longrightarrow$$
 Cu<sup>2+</sup> + 2OH<sup>-</sup>  
 $\therefore$   $K_{sp}$  of Cu(OH)<sub>2</sub> = [Cu<sup>2+</sup>] [OH<sup>-</sup>]<sup>2</sup>  
or  $1.0 \times 10^{-19} = [Cu^{2+}] (1)^2$   
or  $[Cu^{2+}] = 1.0 \times 10^{-19} \text{ M}$ 

The standard electrode potential of Cu<sup>2+</sup>|Cu is represented as follows:  $Cu_{(aa)}^{2+} + 2e^{-} \longrightarrow Cu_{(s)}$ 

Using Nernst equation, 
$$E = E^{\circ} - \frac{0.059}{n} \log \frac{1}{[\text{Cu}^{2+}]}$$
  
=  $0.34 - \frac{0.059}{2} \log \frac{1}{1 \times 10^{-19}}$  [::  $n = 2$ ]  
=  $0.34 - \frac{0.059}{2} \log (10^{19}) = 0.34 - 0.0295 \times 19$   
=  $0.34 - 0.56 = -0.22 \text{ V}$   
NO<sub>2</sub> NH<sub>2</sub> NH<sub>2</sub> NH<sub>2</sub> Rr  $\frac{\text{NH}_2}{\text{Br}}$  Rr

14. (5):

$$(NH_4)_2S$$
 $NO_2$ 
 $NO_2$ 

[k is same]

$$\therefore \frac{r_1}{r_2} = \frac{C_1}{C_2} \therefore \frac{r_1 (\text{at } 10 \text{ min})}{r_2 (\text{at } 20 \text{ min})} = \frac{0.04}{0.03} = \frac{C_1}{C_2}$$

Now  $t = \frac{2.303}{k} \log \frac{C_1}{C_2}$  [For first order reaction]

or 
$$k = \frac{2.303}{t} \log \frac{C_1}{C_2}$$

When, 
$$t = 10 \text{ min}$$
,  $k = \frac{2.303}{10} \log \frac{0.04}{0.03}$ 

or 
$$k = \frac{2.303}{10} \log \frac{4}{3} = 0.0287 \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0287} = 24.15 \,\text{min}$$





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2020

Unit 6

## **Aldehydes, Ketones and Carboxylic Acids**

### **Aldehydes and Ketones**

- **General formula**:  $C_nH_{2n}O$  having C=O group. For ketones, value of  $n \ge 3$ .
  - **Aldehydes**: R = H, alkyl or aryl.
  - **Ketones**: R = R = R Retores: R = R = R Retores: R = R

### Nomenclature :

- The common names of most aldehydes are derived from the common names of the corresponding carboxylic acids by replacing the ending –'ic' of acid with suffix 'aldehyde'.
- The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending -'e' with -'al' and -'one' respectively. e.g.,

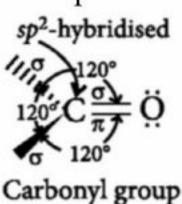
$$CH_3$$
— $C$ — $CH_2$  $CH_3$ ,  $C$ — $CH_3$ ,  $C$ — $CH_3$ ,

Phenylethanone (Acetophenone)

Diphenylmethanone (Benzophenone)

### STRUCTURE

- The C –atom of carbonyl group is sp<sup>2</sup>-hybridised and forms three σ –bonds and one π –bond with O –atom.
- In carbonyl group, carbon and other three atoms lie in the same plane with bond angle of 120°, therefore carbonyl group is planar and  $\pi$ -electron cloud lies above and below of this plane.



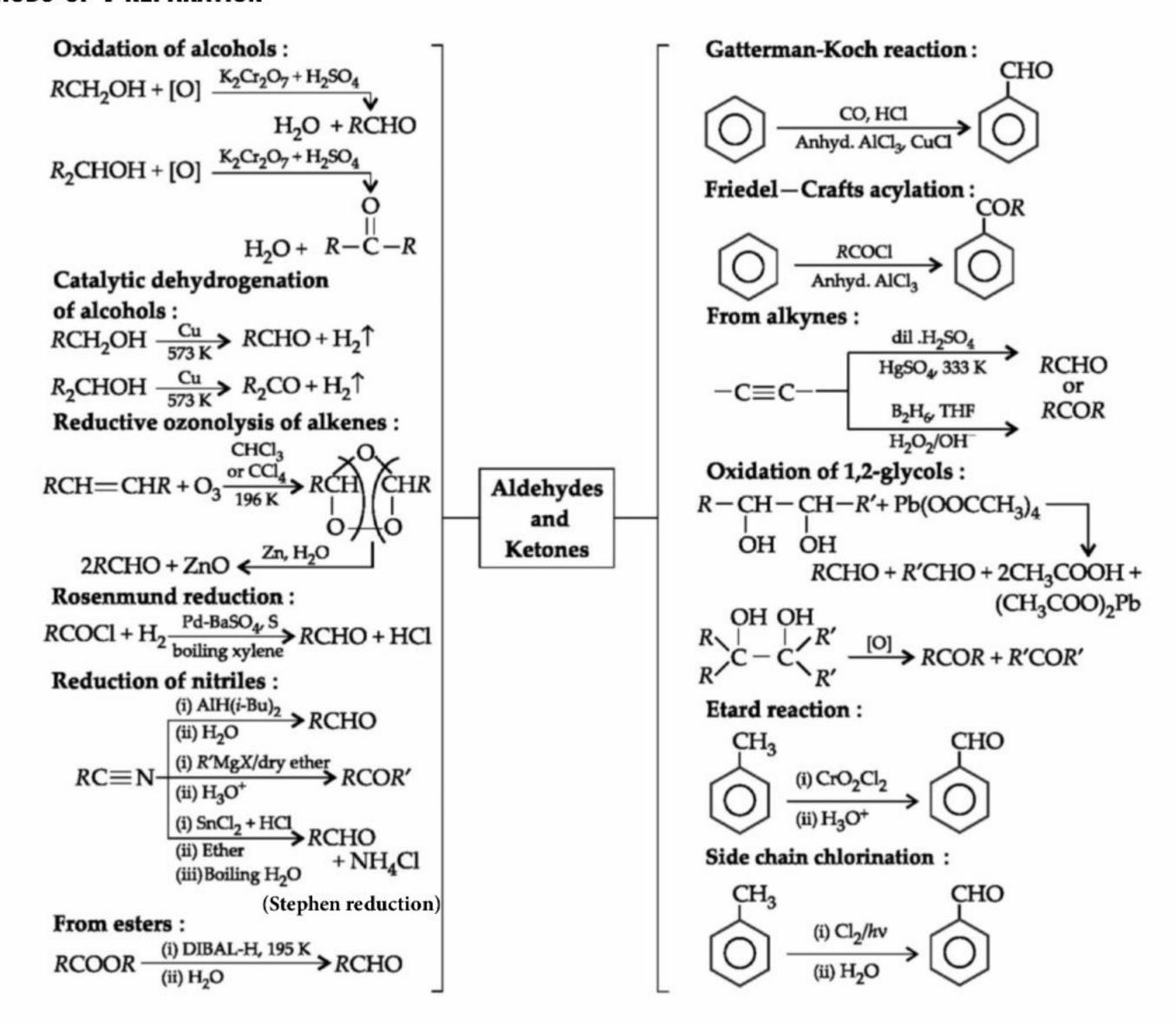
### POLAR NATURE OF CARBONYL GROUP

 In carbonyl group, > C = O bond is stronger, shorter and polarised. As oxygen is more electronegative than carbon, the double bond of carbonyl group is polar and shows dipole moment. Polarisation contributes to the reactivity of aldehydes and ketones.

$$\begin{bmatrix} R \\ R \end{bmatrix} C = \ddot{O}: \longrightarrow R \\ R \downarrow \dot{C} - \ddot{O}: \end{bmatrix}$$

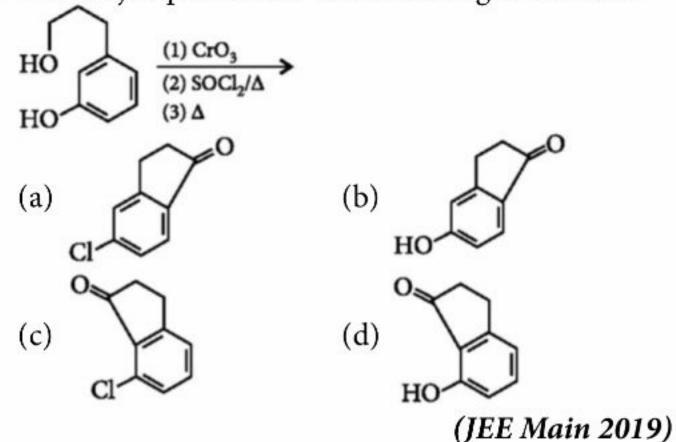
Dipole moment,  $\mu = 2.3-2.8$  D

### METHODS OF PREPARATION



### PEEP INTO PREVIOUS YEARS

1. The major product of the following reaction is



 The correct statement regarding a carbonyl compound with a hydrogen atom on its alphacarbon, is

- (a) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as carbonylation
- (b) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as keto-enol tautomerism
- (c) a carbonyl compound with a hydrogen atom on its alpha-carbon never equilibrates with its corresponding enol
- (d) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as aldehyde-ketone equilibration.

(NEET Phase-I 2016)

### PHYSICAL PROPERTIES

### Physical state and odour :

- Lower members of aldehydes and ketones (upto C<sub>10</sub>) are colourless, volatile liquids except formaldehyde which is gas at ordinary temperature.
- Higher members of aldehydes and ketones are solids with fruity odour.
- Lower aldehydes have unpleasant odour but ketones possess pleasant smell.

### • Boiling points:

- The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses due to intermolecular attraction (weak dipole-dipole interactions).
- Their boiling points are lower than those of alcohols of similar molecular masses because these dipole-dipole interactions are weaker than intermolecular hydrogen bonding between alcohol molecules.
- Among isomeric aldehydes and ketones, ketones have slightly higher boiling points due to the presence of two electron releasing alkyl groups which make carbonyl group more polar.

### Solubility:

- Lower members of aldehydes and ketones (upto C<sub>4</sub>) are soluble in water due to H-bonding between polar carbonyl group and water. However, solubility decreases with increase in molecular mass.
- Aromatic aldehydes and ketones are much less soluble than corresponding aliphatic aldehydes and ketones due to larger hydrocarbon part.
- All carbonyl compounds are fairly soluble in organic solvents.

### CHEMICAL PROPERTIES

### Nucleophilic addition reactions :

Carbonyl carbon is electron deficient hence acts as electrophile. Nucleophile attacks on the electrophilic carbon atom of the carbonyl group from a direction perpendicular to the plane of the molecule.

$$R_1 \stackrel{+\delta}{\underset{R_2}{\longrightarrow}} \stackrel{-\delta}{\underset{C=O}{\longrightarrow}} \stackrel{\text{Slow}}{\underset{R_1}{\longrightarrow}} \stackrel{\text{Nu}}{\underset{R_2}{\longrightarrow}} \stackrel{\text{Fast}}{\underset{H^+}{\longrightarrow}} \stackrel{\text{Nu}}{\underset{R_1}{\longrightarrow}} \stackrel{\text{Nu}}{\underset{R_2}{\longrightarrow}} OH$$

Aldehydes are generally more reactive than ketones towards nucleophilic addition reactions.

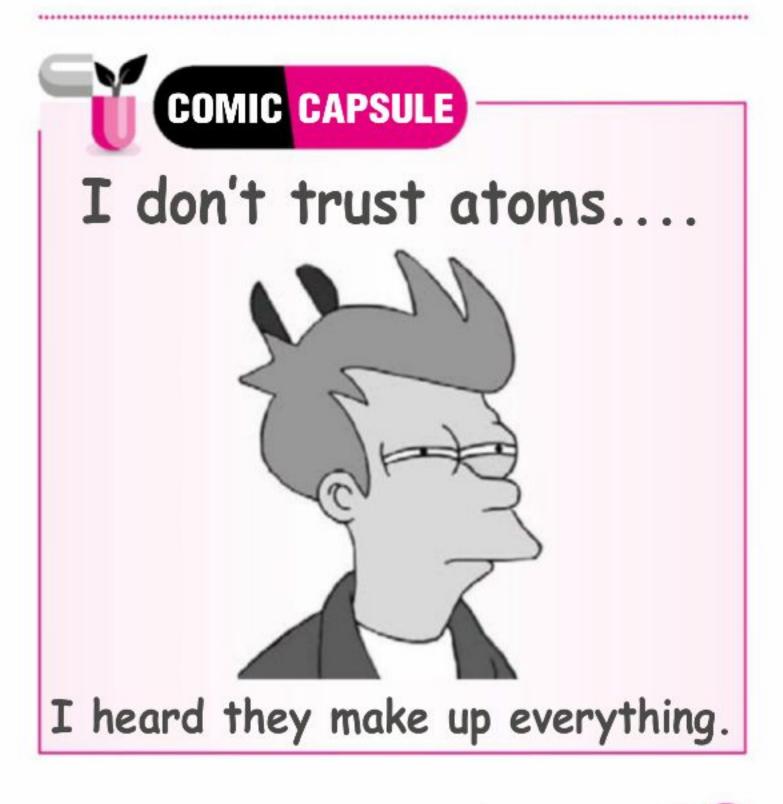
$$C=O \xrightarrow{HCN} COH Cyanohydrin$$

$$C=O \xrightarrow{NaHSO_3} COH SO_3^-Na^+ OH Bisulphite$$

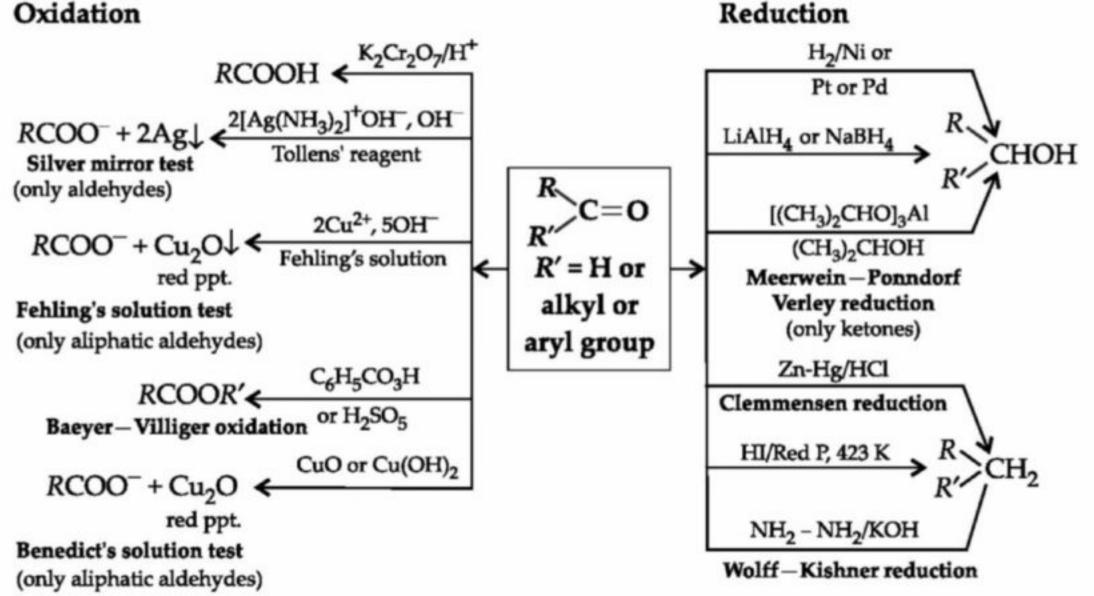
$$C=O \xrightarrow{(i) RMgX} CH_2OH OH$$

$$CH_2OH CH_2OH CH$$

### Nucleophilic addition-elimination reactions :



• Oxidation and reduction reactions:



Haloform reaction :

$$2\text{NaOH} + \text{I}_2 \longrightarrow \text{NaI} + \text{NaOI} + \text{H}_2\text{O}$$
 $R\text{COCH}_3 + 3\text{NaOI} \longrightarrow R\text{COONa} + \text{CHI}_3 \downarrow$ 

$$\text{Iodoform}$$
(yellow ppt.)
$$+ 2\text{NaOH}$$

(Given by compounds having CH<sub>3</sub>CO—group or CH<sub>3</sub>CH(OH)—group).

• Aldol condensation :

$$CH_{3} - C - H + H - CH_{2} - C - H \xrightarrow{\text{dil. NaOH}}$$

$$Acetaldehyde$$

$$O$$

$$H_{3}C - CH - CH_{2} - C - H$$

$$OH$$

$$OH$$

$$3-hydroxybutanal (Aldol)$$

 On heating with dilute acid aldols undergo dehydration to form α, β-unsaturated carbonyl compounds.

 Cross aldol condensation: When condensation takes place between two different aldehydes or ketones, or between one aldehyde and one ketone, it is called as cross aldol condensation.

If both the reactants contain  $\alpha$ -hydrogen atoms then it gives a mixture of four products.

e.g., CH<sub>3</sub>CHO + CH<sub>3</sub>CH<sub>2</sub>CHO 
$$\xrightarrow{1. \text{NaOH}}$$
 CH<sub>3</sub>CH=CH-CHO
Ethanal Propanal  $\xrightarrow{2. \Delta}$  CH<sub>3</sub>CH=CH-CHO
$$+ \text{CH}_3\text{CH}_2\text{CH} = - \text{CHO} + \text{CH}_3\text{CH} = \text{C-CHO}$$

$$CH_3 \qquad CH_3$$

$$2-\text{Methylpent-2-enal} \qquad 2-\text{Methylbut-2-enal}$$

$$+ \text{CH}_3\text{CH}_2\text{CH} = \text{CH-CHO}$$

$$\text{Pent-2-enal}$$

If only one carbonyl compound contains  $\alpha$ -hydrogen then only one product is formed.

 Intramolecular aldol condensation: It takes place in dialdehydes/diketones or compound containing one aldehyde and one ketone group and gives rise to cyclic products.

 Cannizzaro's reaction: It is shown by aldehydes which do not have α-H atom. The aldehydes undergo disproportionation i.e., self oxidationreduction process.

2HCHO 
$$\xrightarrow{50\% \text{ NaOH}}$$
 HCOONa + CH<sub>3</sub>OH  
2C<sub>6</sub>H<sub>5</sub>CHO  $\xrightarrow{50\% \text{ NaOH}}$  C<sub>6</sub>H<sub>5</sub>COONa + C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH

Cross Cannizzaro reaction: It takes place between two different aldehydes to give all possible products. Cross Cannizzaro reaction of formaldehyde with other aldehydes always gives sodium formate and alcohol of other aldehyde.

 Intramolecular Cannizzaro reaction: It is given by dialdehydes having no α-hydrogen atoms in the presence of concentrated alkali solution.

 Tischenko's reaction: All aldehydes (with or without α-hydrogen atom) in presence of aluminium ethoxide, [Al(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>] undergo simultaneous oxidation (to carboxylic acid) and reduction (to alcohol) to form an ester.

$$CH_{3}-CHO+CH_{3}-CHO \xrightarrow{Al(OC_{2}H_{5})_{3}} \\ [CH_{3}-COOH+CH_{3}CH_{2}OH] \\ -H_{2}O \downarrow \Delta \\ O \\ CH_{3}-C-O-C_{2}H_{5}$$

 Benzoin condensation: Two molecules of aromatic aldehyde on heating with alcoholic solution of KCN undergo condensation to produce benzoin.

 Polymerisation: Lower aldehydes readily undergo polymerisation giving different products under different conditions. Polymerization of acetaldehyde also yields different products under different conditions.

Paraldehyde is used as hypnotic, *i.e.*, sleep inducing agent.

Perkin reaction: It is a condensation reaction in which an aromatic aldehyde condenses with aliphatic acid anhydride in presence of sodium salt of same acid to give a condensate which upon hydrolysis yields α,β-unsaturated acid.

$$H - C = O$$

$$H_{2}CH - C$$

$$H_{3}C - C$$

$$O$$

$$Acetic anhydride O O$$

$$H - C = CH - C - O - C - CH_{3}$$

$$H_{2}O/H^{+}$$

$$-CH_{3}COOH$$

$$HC = CH - COOH$$

Cinnamic acid

 Knoevenagel reaction: It involves condensation between active methylene group and carbonyl groups in the presence of base.

$$R \subset C = O + CH_2 < CN_{CN} \frac{\text{pyridine/H}^+/\Delta}{\text{-H}_2O, -CO_2}$$

$$R \subset C = CH - COOH$$

 Reformatsky reaction: It involves the reaction of aldehydes and ketones with α-halogenated ester in presence of Zn to yield β-hydroxy ester.

$$R C = O + Br - CH_{2}COOC_{2}H_{5} \xrightarrow{Zn/ether reflux}$$

$$R C OH OHOR R CH_{2} - C - OC_{2}H_{5} \xrightarrow{R} C CH_{2} - C - OC_{2}H_{5}$$

$$\beta$$
-hydroxy ester O

• Reaction with ammonia: Formaldehyde reacts with ammonia to form hexamethylene tetramine. Nitration of hexamethylene tetramine produces RDX, a well-known explosive.

6HCHO + 4NH<sub>3</sub> 
$$\xrightarrow{-6\text{H}_2\text{O}}$$
  $\Rightarrow$  (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub>  $\xrightarrow{\text{HNO}_3}$  RDX

Hexamethylenetetramine (Urotropine)

 Wittig reaction: It involves the reaction between an aldehyde or ketone and a phosphorus ylide to form alkene.

# CONCEPT MAP

### **ESSENTIALS OF INORGANIC CHEMISTRY (PART I)**

### **General Principles and Processes of Isolation of Elements**

### Metallurgy

- Minerals: Naturally occurring chemical substances in the earth's crust obtainable by mining.
- Ores: The minerals from which metal can be extracted profitably and conveniently.
- Metallurgy: The entire scientific and technological process used for isolation of the metal from its ore.

### Concentration of Ore

The whole process of obtaining a pure metal from its ore.

- Crushing and Grinding (Pulverisation):
   Lumps of ore Crushers Small pieces Ball Fine powder
- Concentration or Benefication of Ore: It is the removal
  of gangue or matrix from the powdered ore. The impurities
  present in an ore are called gangue or matrix.
- Gravity separation or levigation or hydraulic washing:
   For oxide ores, based on difference in the densities of ore (heavier) and gangue particles, using wilfley tables.
- Froth floatation: For sulphide ores, based on perferential wetting of ore (by oil) and gangue (by water).
- Magnetic separation: Based on difference in magnetic properties. (Either ore or the impurities associated with magnetic nature.)
- Leaching: When ore is soluble in a suitable solvents while impurities are not.
- For Al → Baeyer's process : from bauxite ore For Au → Mac-Arthur Forest cyanide process : from argentite ore.

### Thermodynamic Principles of Metallurgy

For a reaction to occur,  $\Delta G$  should be negative. A reaction with  $\Delta G$  positive can be made to occur if it is coupled with another reaction having a large negative  $\Delta G$ , so that the net  $\Delta G$  of both the reactions is positive.

**Ellingham Diagram**: Plots of  $\Delta_r G^{\circ}$  vs T. These help in predicting the feasibility of thermal reduction of an ore to metal.

- Slope = Positive, because ΔG° increases with rise in T.
- Each curve is a straight line except when phase changes take place (s → l, l → g).
- Metal oxide placed higher in the diagram can be reduced by the metal placed lower.

### Metals from Concentrated Ore

- Concentrated Ore: Conversion of concentrated ore into reducible form (oxidation).
  - Calcination: Converting concentrated ore into oxide by heating it strongly below its melting point in the absence of air
  - Roasting: The concentrated ore (usually sulphide) is heated strongly, in the presence of excess of air below its melting point.
- Reduction or conversion of oxides to metals: The ore obtained after calcination or roasting is reduced to metal and choice of reducing agent depends upon the nature of ore.
- Carbon or carbon monoxide is used for oxides of Fe, Cu, Zn, Mg, Co, etc. and the process is called smelting.
- Electropositive metals like Na, Al, Mg or hydrogen are used for reduction of ores of Mn, Cr, Ti, Mo, W, etc.
- Auto-reduction process is used for ores of Pb, Hg, Cu, etc.
- Electrolytic reduction is used for highly electropositive metals.
- Hydrometallurgy or displacement method is used for Ag, Au, etc.

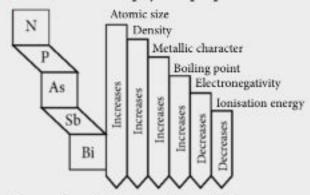
### Refining

Methods	Metals Purified  Used for low melting metals like Sn, Pb, Hg, Bi, etc.		
Liquation			
Distillation	Used for volatile metals like Zn, Hg, Cd, etc., or metals containing non-volatile impurities.		
Poling	Used for metals which contain impurities of their own oxides $e.g.$ , Cu.		
Cupellation	Used for metals containing easily oxidisable impurities $\epsilon$ . $g$ ., Ag containing Pb impurities.		
Electrolytic refining	Used for metals like Cu, Ag, Au, Al which get deposited at cathode and impurities get deposited at anode. Solution of a soluble metal salt acts as an electrolyte.		
Mond's process	Used for refining of Ni.		
Zone refining	Used to produce extremely pure metals (semiconductors) like Si, Ge, Ga, B and In.		
van Arkel method	Used for ultra-pure metals like Ti, Zr which are used in space technology.		

### The p-Block Elements (Group 15 to 18)

### **Group-15 Elements**

- General electronic configuration: ns<sup>2</sup>np<sup>3</sup>
- General trends in physical properties :



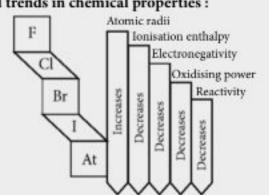
Moscovium (Mc): Atomic no. 115

### **Chemical Properties**

- Hydrides: Form MH<sub>3</sub> type hydrides.
  - Melting point: PH<sub>3</sub> < AsH<sub>3</sub> < SbH<sub>3</sub> < NH<sub>3</sub>
- Boiling point: BiH<sub>3</sub> > SbH<sub>3</sub> > NH<sub>3</sub> > AsH<sub>3</sub> > PH<sub>3</sub>
   Halides: Form MX<sub>3</sub> and MX<sub>5</sub> types of halides.
  - Lewis acid strength: PCl<sub>3</sub> > AsCl<sub>3</sub> > SbCl<sub>3</sub> and
  - Lewis base strength: NI<sub>3</sub> > NBr<sub>3</sub> > NCl<sub>3</sub> > NF<sub>3</sub>

### **Group-17 Elements**

- General electronic configuration : ns<sup>2</sup>np<sup>5</sup>
- General trends in chemical properties :



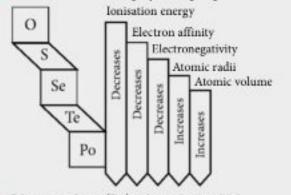
• Tennessine (Ts): Atomic no. 117

### Chemical Properties

- Oxidizing power: F<sub>2</sub> > Cl<sub>2</sub> > Br<sub>2</sub> > l<sub>2</sub>
- Hydrogen halides :
- B.Pt. and M.Pt. : HF > HI > HBr > HCl
- Dipole moment and Thermal stability:
   HF > HCl > HBr > HI
- Bond length, acidic strength and reducing nature :
- HF < HCl < HBr < HI</li>Oxoacids of halogens :
  - Acidic strength: HClO < HClO<sub>2</sub> < HClO<sub>3</sub> < HClO<sub>4</sub>

### **Group-16 Elements**

- General electronic configuration: ns<sup>2</sup>np<sup>4</sup>
- General trends in physical properties :



Livermorium (Lv): Atomic no. 116

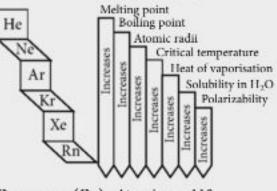
### **Chemical Properties**

- Hydrides: H<sub>2</sub>M type, where M is sp<sup>3</sup> hybridised.
- M.Pt. and B.Pt. : H<sub>2</sub>O > H<sub>2</sub>Te > H<sub>2</sub>Se > H<sub>2</sub>S
- Thermal stability: H<sub>2</sub>O > H<sub>2</sub>S > H<sub>2</sub>Se > H<sub>2</sub>Te
- Volatility: H<sub>2</sub>O < H<sub>2</sub>Te < H<sub>2</sub>Se < H<sub>2</sub>S
   Reducing power: H<sub>2</sub>O < H<sub>2</sub>S < H<sub>2</sub>Se < H<sub>2</sub>Te
- Reducing power: H<sub>2</sub>O < H<sub>2</sub>S < H<sub>2</sub>Se < H<sub>2</sub>Te
   Bond angle and dipole moment:
- Bond angle and dipole moment :
   H<sub>2</sub>Te < H<sub>2</sub>Se < H<sub>2</sub>S < H<sub>2</sub>O
- Halides: Form MX<sub>6</sub>, MX<sub>4</sub> and MX<sub>2</sub> types of halides.
  - Dihalides: All elements except selenium form dihalides.
     Tetrahalides: SF<sub>4</sub>(gas), SeF<sub>4</sub>(liquid), TeF<sub>4</sub> (solid). SF<sub>4</sub>
  - is readily hydrolysed than SF<sub>6</sub>.
- Oxyhalides: Only S and Se form oxyhalides.

  Oxides: SO<sub>2</sub> and SeO<sub>2</sub>; SO<sub>3</sub>, SeO<sub>3</sub> and TeO<sub>3</sub>: Acidic
- Oxides: SO<sub>2</sub> and SeO<sub>2</sub>; SO<sub>3</sub>, SeO<sub>3</sub> and TeO<sub>3</sub>: Acidis
   TeO<sub>2</sub> and PoO<sub>2</sub>: Amphoteric
  - 1eO<sub>2</sub> and PoO<sub>2</sub>: Amphoteric

### Group-18 Elements

- General electronic configuration : ns<sup>2</sup>np<sup>6</sup>
- General trends in physical properties :



• Oganesson (Og) : Atomic no. 118

### Chemical Properties B.Pt. are very low.

- M.Pt. and B.Pt. are very low.
   Ionisation enthalog: He > N
- Ionisation enthalpy: He > Ne > Ar > Kr > Xe > Rn

### Distinction between aldehydes and ketones:

Tests	Aldehydes	Ketones
Schiff's reagent	Pink colour	No colour
Fehling's solution	Red precipitate	No precipitate
Tollens' reagent	Silver mirror	No silver mirror
2,4- dinitrophenyl- hydrazine	Orange-yellow or red well defined crystals with melting points characteristic of individual aldehydes.	Orange-yellow or red well defined crystals with melting points characteristic of individual ketones.

### PEEP INTO PREVIOUS YEARS

Choose the correct option(s) for the following reaction sequence.

(d) 
$$CO_2H$$
  $MeO$   $Q$   $MeO$   $Q$ 

MeO

(JEE Advanced 2019)

The major product B formed in the following reaction sequence is

Of the following, which is the product formed when cyclohexanone undergoes aldol condensation followed by heating?

- Reaction of a carbonyl compound with one of the following reagents involves nucleophilic addition followed by elimination of water. The reagent is
  - (a) hydrazine in presence of feebly acidic solution
  - (b) hydrocyanic acid
  - (c) sodium hydrogen sulphite
  - (d) a Grignard reagent.

(AIPMT 2015)

### Points For Extra Scoring

LiAlH<sub>4</sub> is more powerful reducing agent than NaBH<sub>4</sub> as beside aldehydes and ketones it also reduces acids, acid chlorides, esters, amides, anhydrides, nitriles, oximes, alkyl halides, alkyl azides, alkyl tosylates and nitro compounds. LiAlH<sub>4</sub> and NaBH<sub>4</sub> do not reduce isolated double bonds.

MeO

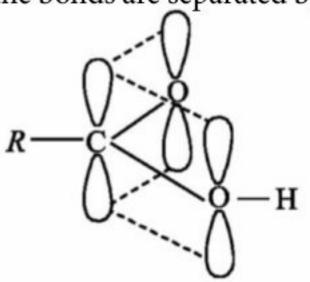
- Formaldehyde cannot be prepared by Rosenmund's reduction since formyl chloride is unstable at room temperature.
- α-Hydroxy ketones reduce Tollens' reagent, Fehling's and Benedict's solution.
- > Haloform reaction can be used to oxidise
- $\alpha$ ,  $\beta$ -unsaturated methyl ketones to  $\alpha$ ,  $\beta$ -unsaturated acids without oxidising double bond.
- Oxidation of methyl ketones is governed by Popoff's rule, according to which carbonyl group of the unsymmetrical ketone remains with the smaller alkyl group.

### Carboxylic Acids

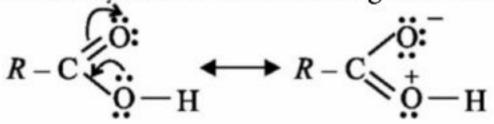
- **General Formula** :  $C_nH_{2n}O_2$  having —COOH group or *R*COOH where, *R*=H or alkyl or aryl.
- Nomenclature:
  - The common names end with the suffix -'ic acid' and have been derived from Latin or Greek names of their natural sources.
  - In the IUPAC system, aliphatic carboxylic acids are named by replacing the ending -'e' in the name of the corresponding alkane with -'oic acid'. In numbering the carbon chain, the carboxylic carbon is numbered one.

### STRUCTURE

Carbon-atom of carboxyl group is sp<sup>2</sup>-hybridised and forms one σ-bond with each oxygen atom and one σ-bond with hydrogen or carbon atom depending upon the structure of carboxylic acid. Half-filled p-orbital of each oxygen atom and unhybridised p-orbital of carbon-atom lie in the same plane and overlap to form a π-bond which is delocalised between three atoms, one carbon and two oxygen atoms. Thus, the bonds are separated by about 120°.



 Thus, carboxylic acid (RCOOH) can be represented as resonance hybrid of the following structures,



due to which the carboxyl carbon is less electrophilic than carbonyl carbon.

### **CLASSIFICATION**

- On the basis of the group to which —COOH group is attached:
  - Aliphatic carboxylic acid : R C OH (where, R = H atom or alkyl group).
  - Aromatic carboxylic acid : Ar C OH(where, Ar = Aryl group)
- On the basis of number of —COOH groups in their molecule:

No. of —COOH group

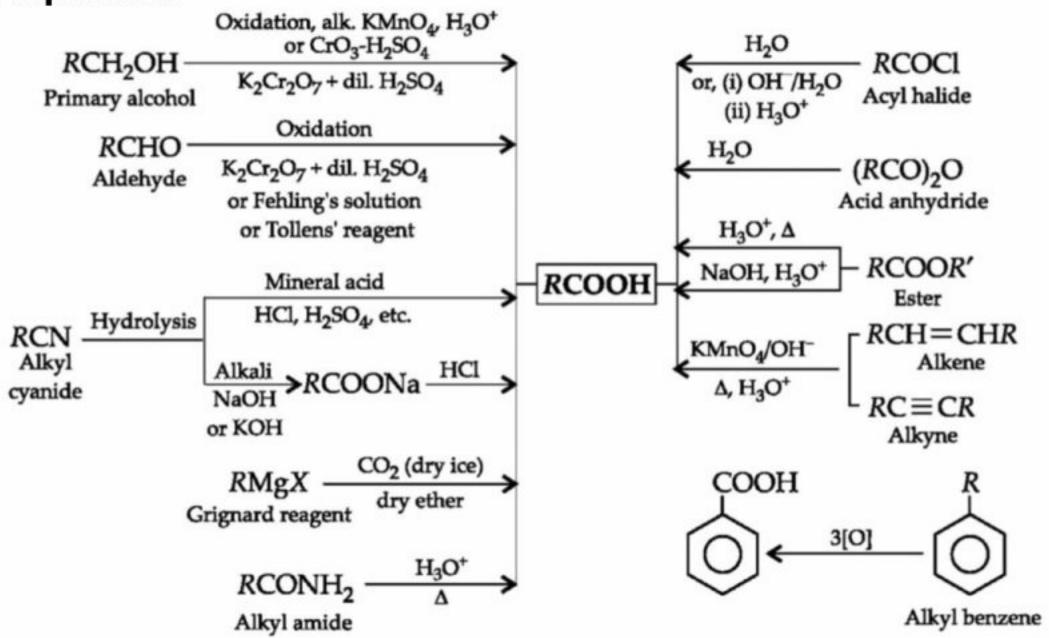
- Monocarboxylic acids: 1
- Dicarboxylic acids: 2
- Tricarboxylic acids: 3
- Saturated and unsaturated monocarboxylic acids are also called fatty acids, because higher acids like palmitic acid, steric acid, oleic acid, etc. were obtained by hydrolysis of fats and oils.

# Quotable Quote 99

Don't read success stories, you will get only message...
Read failure stories, you will get some ideas to get success..!!

A.P.J. ABDUL KALAM

### **Methods of Preparation**



### PHYSICAL PROPERTIES

- Acids upto C<sub>10</sub> are liquids with unpleasant odour.
   The higher members are colourless waxy solids.
- Boiling points: Boiling points of acids increase regularly with molecular weight and higher than alcohols (of comparable molecular mass) due to formation of dimer through H-bonding

$$R = \begin{cases} \delta^{-} & \delta^{+} \\ O & H^{-}O \\ -H^{-}O \\ \delta^{+} & \delta^{-} \end{cases}$$

- Solubility: Acids upto C<sub>4</sub> are completely soluble in water due to H-bonding. Solubility regularly decreases rapidly due to increase in hydrophobic character of alkyl group.
- Melting points: The melting point of an acid containing even number of carbon atoms is always higher homologues containing than the next lower and higher odd number of carbon atoms (alternation effect or oscillation effect) due to effective crystal lattice being symmetrical in nature.

Molecules with even number of C-atoms fit well into the crystal lattice, thus the melting point of these acids is higher. In higher members, the melting point increases with increase in molecular mass. The aromatic acids have higher melting points than the corresponding aliphatic acids.

### CHEMICAL PROPERTIES

• Reactions involving cleavage of O—H bond:

$$R-C-OH$$

Reactions involving cleavage of C—OH bond:

$$R-C-OH \xrightarrow{\text{conc. } H_2SO_4 \\ -H_2O} RCOOR'$$

$$R-C-OH \xrightarrow{\text{r'OH/H}^+ \\ -H_2O} RCOOR'$$

$$RCOCl_2 \text{ in pyridine } RCOCl$$

$$RCOCl_2 \text{ in pyridine } RCONH_2$$

$$RCONH_2$$

$$Amide$$

Reactions involving —COOH group:

(i) LiAlH<sub>4</sub>/ether or B<sub>2</sub>H<sub>6</sub>/
ether

$$R-C-OH$$

(ii) H<sub>3</sub>O<sup>+</sup>

(Reduction)

NaOH/CaO

 $\Delta$ 
 $RH + Na_2CO_3$ 

(Decarboxylation)

 Hell-Volhard-Zelinsky reaction: Aliphatic carboxylic acids on reaction with bromine or chlorine in presence of small amount of red phosphorous produces α-halo acids.

$$RCH_{2}COOH \xrightarrow{(i) X_{2}/Red P} R - CH - COOH$$

$$X$$

$$\alpha-Halocarboxylic acid$$

 Ring substitution in aromatic acids: Aromatic carboxylic acids undergo electrophilic substitution reactions in which the carboxyl group acts as a deactivating and meta directing group.

Distinction between phenol and carboxylic acid

Test	Phenol	Carboxylic acid
NaHCO <sub>3</sub> test	No reaction	Brisk effervescence of CO <sub>2</sub> gas
FeCl <sub>3</sub> test	Violet colour	Buff coloured ppt.

### PEEP INTO PREVIOUS YEARS

7. The major product of the following reaction is

CH<sub>3</sub>
COCH<sub>3</sub>
(i) KMnO<sub>4</sub>/KOH, 
$$\Delta$$
(ii) H<sub>2</sub>SO<sub>4</sub>(dil.)

COCH<sub>3</sub>
(b) HOOC

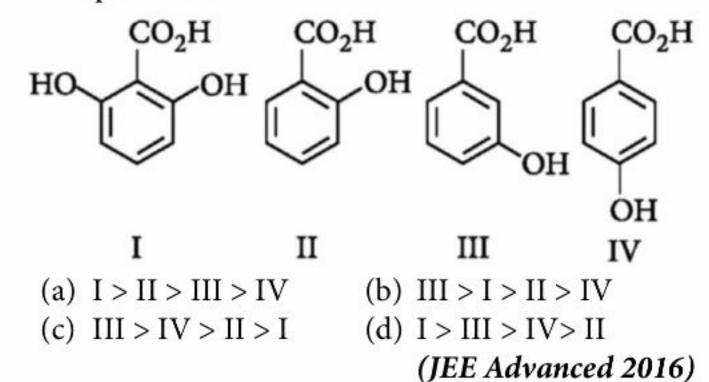
COCOOH
(c) OHC

COCOOH
(d) HOOC

(JEE Main 2019)

8. The major product of the following reaction is

- Carboxylic acids have higher boiling points than aldehydes, ketones and even alcohols of comparable molecular mass. It is due to their
  - (a) formation of intramolecular H-bonding
  - (b) formation of carboxylate ion
  - (c) more extensive association of carboxylic acid via van der Waals' forces of attraction
  - (d) formation of intermolecular H-bonding. (NEET 2018)
- 10. The correct order of acidity for the following compounds is



### Points For Extra Scoring

- Methanoic acid and its sodium salt act as a reducing agent and reduces Tollens' reagent, Fehling's solution and KMnO<sub>4</sub>.
- Acidic strength of acids: Benzoic acid  $(K_a = 6.5 \times 10^{-5})$  is somewhat stronger than simple aliphatic acids. This is because in benzoic acid the carboxyl group is attached to more electronegative  $sp^2$  hybridised carbon as compared to less electronegative  $sp^3$  hybridised carbon in aliphatic acids.
  - Electron withdrawing groups (EWG's) make acids stronger.

$$G \leftarrow C$$
 $O \rightarrow H$ 

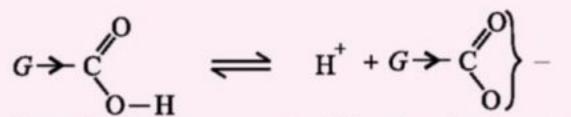
electron withdrawing group

Stabilises the carboxylate

G is electron withdrawing group (EWG)

Stabilises the carboxylate anion, increases acidity

 Electron donating groups (EDG's) make acids weaker.



G is electron donating group (EDG)

Destabilises the carboxylate anion, decreases acidity

– I effect increases with increasing number of EWG's.

 $F_3CCOOH > F_2CHCOOH > FCH_2COOH$ Strongest acid

> CH<sub>3</sub>COOH

Weakest acid

 – I effect decreases with increasing distance from the EWG.

$$\begin{array}{c} \text{CH}_3\text{CH}_2-\text{CH}-\text{COOH} > \text{CH}_3\text{CH}-\text{CH}_2-\text{COOH} \\ \text{F} \\ \text{Strongest acid} \end{array}$$

> FCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>—COOH Weakest acid

 ± R effect on aromatic ring decreases or increases acidity.

### **Answer Key For Peep Into Previous Years**

- . (b
  - **(b)**
- 2
- **(b)**
- 3.
- (a, d)
- 4.
- 5

(c)

- (a)

(a)

7. (a) 8. (c) 9. (d) 10. (a)

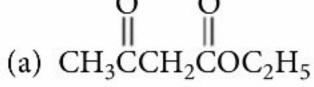


- 1. The reagent with which both acetaldehyde and acetone react easily is
  - (a) Fehling's reagent
- (b) Grignard reagent
- (c) Schiff's reagent
- (d) Tollens' reagent.
- 2.  $C_6H_{10}O_3$  (keto ester)  $\xrightarrow{\text{NaOH} + I_2}$  yellow ppt. + B

  (A)

$$B \xrightarrow{H^+} C \xrightarrow{\Delta} CH_3COOH.$$

Hence, A is





- (b) CH<sub>3</sub>CH<sub>2</sub>CCH<sub>2</sub>COCH<sub>3</sub>
- (c) both of these
- (d) none of these.
- 3. 3-Hydroxybutanal is formed when (X) reacts with
  - (Y) in dilute (Z) solution. What are X, Y and Z?
  - (a) CH<sub>3</sub>CHO, (CH<sub>3</sub>)<sub>2</sub>CO, NaOH
  - (b) CH<sub>3</sub>CHO, CH<sub>3</sub>CHO, NaCl
  - (c) (CH<sub>3</sub>)<sub>2</sub>CO, (CH<sub>3</sub>)<sub>2</sub>CO, HCl
  - (d) CH<sub>3</sub>CHO, CH<sub>3</sub>CHO, NaOH
- 4. Which of the following compounds has wrong IUPAC name?

- (a) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>COOCH<sub>2</sub>CH<sub>3</sub> Ethyl butanoate
- (b) CH<sub>2</sub>—CH<sub>2</sub> | | | HOOC COOH 2-Methyl-3-butanol
- (c) CH<sub>3</sub>—CH—CH<sub>2</sub>CHO | CH<sub>3</sub>

3-Methylbutanal

- 5. *m*-Chlorobenzaldehyde on reaction with concentrated KOH at room temperature gives
  - (a) potassium *m*-chlorobenzoate and *m*-hydroxy benzaldehyde
  - (b) *m*-hydroxy benzaldehyde and *m*-chlorobenzyl alcohol
  - (c) *m*-chlorobenzyl alcohol and *m*-hydroxybenzyl alcohol
  - (d) potassium *m*-chlorobenzoate and *m*-chlorobenzyl alcohol.

(c) 
$$\left\langle \begin{array}{c} O \\ CH_3 \\ CH_3 \end{array} \right\rangle$$

- Which of the following is used as lachrymator or tear gas?
- (a) C<sub>6</sub>H<sub>5</sub>COCl (b) C<sub>6</sub>H<sub>5</sub>OC<sub>6</sub>H<sub>5</sub> (c) C<sub>6</sub>H<sub>5</sub>COCH<sub>2</sub>Cl (d) C<sub>6</sub>H<sub>5</sub>COCH<sub>3</sub>
- 8. The end product of the following reaction is

$$CH_{3}CCH_{2}CH_{2}CH_{2}CO_{2}H \xrightarrow{1. \text{ NaBH}_{4}} CH_{2}O, H^{+}$$

$$CH_{2}$$

(a) 
$$O = O$$
 (b)  $O = O$  (c)  $O = O$ 

- Which one of the following is not correct?
  - C=O Clemmensen's reduction
  - Wolff-Kishner reduction
  - (c)  $-\text{COCl} \xrightarrow{\text{Rosenmund's reduction}} -\text{CHO}$
  - (d)  $-c \equiv N$  Stephen's reduction
- 10. The final product of the following sequence of reactions is

$$(CH_3O)_2CHCH_2CH_2CH_2Br \xrightarrow{Mg} \xrightarrow{H_2C=O} \xrightarrow{Heat} \xrightarrow{H_3O^+} O$$

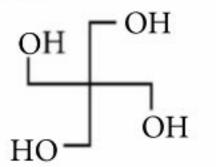
(a) CH<sub>3</sub>OCCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH

- (c) HCCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH<sub>3</sub>
- (d) HCCH2CH2CH2CH3

What is *B*?

- (a) CH<sub>3</sub>CH<sub>2</sub>COCl (b) CH<sub>3</sub>CH<sub>2</sub>CHO
- (c)  $CH_2 = CHCOOH$
- (d) ClCH<sub>2</sub>CH<sub>2</sub>COOH
- 12. Aldehyde group can be protected
  - (a) by acetal formation against attack by alkaline oxidising agents
  - (b) by mercaptal formation against attack by acidic oxidsing agents
  - (c) by both (a) and (b)
  - (d) by none of the above.
- 13. Benzophenone can be converted into benzene using
  - (a) fused alkali
  - (b) anhydrous AlCl<sub>3</sub>
  - (c) sodium amalgam in water
  - (d) acidified dichromate.
- 14. The number of aldol reaction(s) that occur in the given transformation is

$$CH_3CHO + 4HCHO \xrightarrow{conc. aq. NaOH}$$



(a) 1

(b) 2

(c) 3

- (d) 4
- 15. The general formula  $C_nH_{2n}O_2$  could be for open chain
  - (a) diketones
- (b) carboxylic acids
- diols (c)
- (d) dialdehydes.

16. 
$$COCH_3 \xrightarrow{(i) \text{ KOBr, } \Delta} A$$
, The product  $A$  is  $CH_3 \xrightarrow{(ii) H+} \Delta$ 

(a) 
$$COCH_3$$
 (b)  $CH_3$ 

- 17. Which of the following statements regarding chemical properties of acetophenone are wrong?
  - It is reduced to methyl phenyl carbinol by sodium and ethanol.
  - II. It is oxidised to benzoic acid with acidified  $KMnO_4$ .

- III. It does not undergo electrophilic substitution like nitration at *meta*-position.
- IV. It does not undergo iodoform reaction with iodine and alkali.
- (a) I and II
- (b) II and IV
- (c) III and IV
- (d) I and II
- 18. In this reaction,

CH<sub>3</sub>CHO + HCN 
$$\longrightarrow$$
 CH<sub>3</sub>CH(OH)CN  $\xrightarrow{\text{H}_2\text{O/H}^+}$  CH<sub>3</sub>CH(OH)COOH

an asymmetric centre is generated. The acid obtained would be

- (a) 20% d + 80% l-Isomer
- (b) d-Isomer
- (c) l-Isomer
- (d) 50% d + 50% l-Isomer.
- 19. The increasing order of the rate of HCN addition to compounds I to IV is
  - I. HCHO
- II. CH<sub>3</sub>COCH<sub>3</sub>
- III. PhCOCH<sub>3</sub>
- IV. PhCOPh
- iii. Fiicociig
- (a) I < II < III < IV (b) IV < II < III < I
- (c) IV < III < II < I
- (d) III < IV < II < I
- 20. The carboxyl functional group (—COOH) is present in
  - (a) picric acid
- (b) barbituric acid
- (c) ascorbic acid
- (d) aspirin.

### SOLUTIONS

1. (b): Fehling's solution, Schiff's reagent and Tollens' reagent react only with aldehydes, but Grignard reagent reacts with both aldehydes and ketones.

$$\begin{array}{ccc}
O \\
| & OMgBr & OH \\
R - C - R + R'MgBr & \longrightarrow R - C - R & \longrightarrow R - C - R \\
& & & | & & | \\
R' & & & R'
\end{array}$$

2. (a): A yellow precipitate shows a positive iodoform

test. Thus, presence of  $CH_3^{II}$  –group is confirmed. This keto group is at  $\beta$ -position w.r.t. ester, the  $\beta$ -ketoester can be represented as

Thus, R (by difference) is  $C_2H_5$ . Thus,  $\beta$ -keto ester is

$$CH_{3}CCH_{2}COC_{2}H_{5} \xrightarrow{NaOH/I_{2}} CONa \xrightarrow{H^{+}} CONa \xrightarrow{H^{+}} CONa \xrightarrow{H^{+}} CONa \xrightarrow{(A)} CH_{3}COOH \xleftarrow{\Delta} CH_{2}(COOH)_{2}$$

- 4. (b)
- 5. (d): It is an example of Cannizzaro's reaction.

6. (c): 
$$\overset{1}{C}H_{3}\overset{2}{C}\overset{3}{C}H_{2}\overset{4}{C}H_{2}\overset{5}{C}H_{2}\overset{C}{C}H_{2}\overset{C}{C}H_{2}\overset{C}{C}H_{2}\overset{C}{C}H_{3}$$

$$\overset{4}{H_{2}\overset{7}{C}_{2}}\overset{3}{-\overset{7}{C}H_{2}\overset{1}{C}H_{3}}\overset{1}{-\overset{7}{C}H_{3}\overset{2}{C}-\overset{3}{C}H_{2}\overset{4}{C}H_{2}\overset{5}{C}H_{2}}\overset{6}{-\overset{7}{C}H_{2}\overset{7}{C}H$$

- 7. (c): Phenacyl chloride is used as 'tear gas'.
- 8. (a):  $CH_3CCH_2CH_2CO_2H \xrightarrow{NaBH_4}$

CH<sub>3</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H 
$$\xrightarrow{\text{H}_2O/H}^+$$
 Intramolecular esterification  $\xrightarrow{\text{H}_2C}$  O

- 9. (b):  $\gt{C=O} \xrightarrow{\text{Wolff-Kishner reduction}} \gt{CH_2}$ 10. (c):  $(CH_3O)_2CH(CH_2)_3Br \xrightarrow{Mg/ether}$
- 10. (c):  $(CH_3O)_2CH(CH_2)_3Br \xrightarrow{Mg/ether}$   $(CH_3O)_2CH(CH_2)_3MgBr \xrightarrow{HCHO/H_3O^+}$  $(CH_3O)_2CH(CH_2)_3CH_2OH \xrightarrow{\Delta}OHC(CH_2)_4OH$
- 11. (c):  $CH_3CH_2COOH \xrightarrow{Cl_2} CH_3CHClCOOH \xrightarrow{Red P} (A)$   $\xrightarrow{-HCl} CH_2 CHCOOH \xrightarrow{-HCl} CH_2 CHCOOH (B)$
- 12. (c)

### 13. (a):

### 14. (c):

$$H_{3}C-C-H \xrightarrow{(ii) OH^{-}} HO-CH_{2}-CH_{2}-CH=O$$

$$(Aldol) OH$$

$$CH_{2}$$

$$HO-CH_{2}-C-CHO \xrightarrow{(ii) HCHO} (Aldol)$$

$$OH$$

$$CH_{2}$$

$$HO-CH_{2}-C-CHO \xrightarrow{(ii) OH^{-}} (Aldol)$$

$$OH$$

$$CH_{2}$$

$$C$$

### 15. (b)

16. (b): 
$$COCH_3$$
 (i) KOBr,  $\Delta$  (ii) H<sup>+</sup> (haloform test)

 $CH_3$   $COOH$  +  $CHBr_3$   $COOH$ 

18. (d): Since  $\searrow_{C=O}$  group is planar, nucleophile can attack carbonyl group from either direction and hence a racemic mixture (50% d + and 50% l - isomer) is obtained in product.

9. (c): The ketones are less reactive as compared to aldehydes due to +I- effect of alkyl groups. Aromatic aldehydes and ketones are less reactive than their corresponding aliphatic analogous and alkyl-aryl ketones are more reactive than diaryl ketones. Therefore, option (c) is correct.

20. (d): 
$$O_2N$$
  $O_2$   $O_2N$   $O_3$   $O_4$   $O_5$   $O_5$ 

# For the SCIENTIST in

### Artificial leaf' successfully produces clean gas

Awidely-used gas that is currently produced from fossil fuels can instead be made by an 'artificial leaf' that uses only sunlight, carbon dioxide and water, and which could eventually be used to develop a sustainable liquid fuel alternative to gasoline.

The carbon-neutral device sets a new benchmark in the field of solar fuels, researchers demonstrated that it can directly produce the gas called syngas in a sustainable and simple way. The gas is used to produced a range of commodities, such as fuels, pharmaceuticals, plastics and fertilisers.

Rather than running on fossil fuels, the artificial leaf is powered by sunlight, although it still works efficiently in cloudy and overcast days. And unlike the current industrial processes for producing syngas, the leaf does not release any additional carbon dioxide into the atmosphere. The results are reported in the journal Nature Materials.

On the artificial leaf, two light absorbers, similar to the molecules in plants that harvest sunlight, are combined with a catalyst made from the naturally abundant element cobalt. When the device is immersed in water, one light absorber uses the catalyst to produce oxygen. The other carries out the chemical reaction that reduces carbon dioxide and water into carbon monoxide and hydrogen, forming the syngas mixture.

Chapterwise practice questions for CBSE Exams as per the latest pattern and marking scheme issued by CBSE for the academic session 2019-20.

Series 7

Biomolecules, Polymers, Chemistry in Everyday Life

Time Allowed: 3 hours Maximum Marks: 70

### **GENERAL INSTRUCTIONS**

- (i) All questions are compulsory.
- (ii) Section A: Q.no. 1 to 20 are very short answer questions (objective type) and carry 1 mark each.
- (iii) Section B: Q.no. 21 to 27 are short answer questions and carry 2 marks each.
- (iv) Section C: Q.no. 28 to 34 are long answer questions and carry 3 marks each.
- (v) Section D: Q.no. 35 to 37 are also long answer questions and carry 5 marks each.
- (vi) There is no overall choice. However an internal choice has been provided in two questions of two marks, two questions of three marks and all the three questions of five marks weightage. You have to attempt only one of the choices in such questions.
- (vii) Use log tables if necessary, use of calculators is not allowed.

### **SECTION-A**

# Read the given passage and answer the questions 1 to 5 that follow:

Natural rubber or raw rubber consists of basic material latex which is a dispersion of isoprene. During the treatment this isoprene forms a high molecular weight polymer of isoprene. Majority of the synthetic rubbers are derived from butadiene derivatives. Some important synthetic rubbers are neoprene, Buna-S, Buna-N and thiokol.

- 1. How is natural rubber prepared?
- Define vulcanisation of rubber.
- 3. Name the fillers used in crude rubber and why they are used so?
- 4. What is Buna-S?
- 5. What is Buna-N?

### Questions 6 to 10 are one word answers:

6. What is the name given to the linkage that holds the amino acids together in proteins?

- 7. To which category, does vulcanised rubber belong?
- Name a watersoluble vitamin which is a powerful antioxidant.
- 9. Name the artificial sweetener which has highest sweetness value in comparison to cane sugar.
- 10. Write the name of one of the common initiators used in free radical addition polymerisation.

### Questions 11 to 15 are Multiple choice questions:

- 11. Polymer formation from monomers starts by
  - (a) condensation reaction between monomers
  - (b) coordination reaction between monomers
  - (c) conversion of monomer to monomer ions by protons
  - (d) hydrolysis of monomers.
- 12. Which of the following is a common antacid?
  - (a) NaOH
  - (b)  $Ca(OH)_2$
  - (c)  $Mg(OH)_2$
  - (d) KOH

- 13. Complete hydrolysis of cellulose gives
  - (a) *D*-fructose
- (b) *D*-ribose
- (c) D-glucose
- (d) L-glucose.
- 14. Carbohydrates are stored in human body as the polysaccharide
  - (a) maltose
- (b) glycogen
- (c) cellulose
- (d) amylose.
- 15. An ester used as medicine is
  - (a) ethyl acetate
- (b) methyl acetate
- (c) methyl salicylate
- (d) ethyl benzoate.

### Questions 16 to 20:

- (a) Both assertion and reason are correct statements, and reason is the correct explanation of the assertion.
- (b) Both assertion and reason are correct statements, but reason is not the correct explanation of the assertion.
- (c) Assertion is correct, but reason is wrong statement.
- (d) Assertion is wrong, but reason is correct statement.
- **16. Assertion**: Nylon 6, 6 is a thermoplastic polymer. Reason: It is prepared by condensation polymerisation of hexamethylenediamine and adipic acid.
- 17. Assertion: Acid or enzymatic hydrolysis of sucrose to give an equimolar mixture of D (+) glucose and D (-) fructose is called inversion.

Reason: Sucrose is the only naturally occurring disaccharide which is reducing sugar.

- 18. Assertion: Penicillin is an antibiotic.
  - Reason: The drugs which act on the central nervous system and help in reducing anxiety are called antibiotics.
- 19. Assertion: PHBV is an example of biodegradable polymer.

Reason: PHBV is used in speciality packaging, orthopaedic devices, etc.

20. Assertion: Ofloxacin is a bactericidal type of antibiotic.

**Reason**: Ofloxacin has killing effect on microbes.

### **SECTION-B**

- 21. Why is glucose or sucrose soluble in water but cyclohexane or benzene insoluble in water?
- 22. Write the structures of the monomers of the following polymers:

(a) 
$$\left\{\begin{matrix} H & H & O & O \\ I & I & I & O \\ N - (CH_2)_6 - N - C - (CH_2)_4 - C \end{matrix}\right\}_n$$

(b) 
$$\left\{ O - CH_2 - CH_2 - O - C - C - C \right\}_n$$

23. What are natural and synthetic polymers? Give two examples of each type.

How does the presence of double bonds in natural rubber molecules influence their structure and reactivity?

- 24. (a) A child when dropped his soap in a bathing tub, the soap did not sink but was floating. Suggest the method of manufacturing such soap.
  - (b) Give one example and structure of anionic detergent.
- 25. Enumerate the reactions of glucose which cannot be explained by its open chain structures.

- (a) Amino acids show amphoteric behaviour. Why?
- (b) Write one difference between α-helix and β-pleated structures of proteins. (2018)
- 26. (a) Sleeping pills are recommended by doctors to the patients suffering from sleeplessness but it is not advisable to take its doses without consultation with the doctor. Why?
  - (b) Which class of drugs is used in sleeping pills?
- 27. Arrange the following alkenes towards increasing order of reactivity in cationic polymerisation:

$$H_2C = CHCH_3$$
,  $CICH = CH_2$ ,  
 $H_2C = CHC_6H_5$ ,  $H_2C = CHCOOCH_3$ 

### **SECTION-C**

- 28. (a) Answer the following:
  - (i) Can ethylene be polymerised by the cationic process?
  - (ii) Is polyvinyl alcohol soluble in water?
  - (b) Give the structures of each of the products in the following reaction:

$$\begin{array}{c}
\text{NOH} \\
& \xrightarrow{\text{H}^+} C \xrightarrow{\text{polymerisation}} +D + \\
& \xrightarrow{n}
\end{array}$$

- 29. Write the products in each of the following reactions:

  - (i) Sucrose  $\xrightarrow{H^+} A + B$ (ii)  $nCl CH_2 CH_2 Cl + nNa_2S_4 \xrightarrow{Mg(OH)_2} \xrightarrow{Polymerisation}$

### OR

- (a) Differentiate between nucleotide of DNA and RNA.
- (b) The melting point and solubility in water of amino acids are generally higher than that of the corresponding halo acids. Explain.
- **30.** (a) (i) Why is bithional added in soap?
  - (ii) Why are soaps biodegradable whereas detergents are non-biodegradable?

(Delhi 2019)

(b) Define the following term with a suitable example: Artificial sweeteners.

(Delhi 2019, AI 2019)

### OR

- (a) What are fillers and what role these fillers play in soap?
- (b) How are synthetic detergents better than soaps?
- 31. (a) Write down the heterogeneous catalyst involved in the polymerisation of ethylene.
  - (b) Define the term, 'homopolymerisation' giving an example.
- 32. State the significance of primary and secondary structures of proteins.
- 33. (i) Give one example of thermosetting and thermoplastic polymer.
  - (ii) Write the monomers of the following polymer:

- (iii) What is the role of sulphur in vulcanization of rubber?
- 34. (a) What is the basic structural difference between starch and cellulose?
  - (b) Give an example of anomers.

### **SECTION-D**

35. (a) Aspartame, an artificial sweetener, is a peptide and has the following structure:

and has the following structure: 
$$\begin{array}{c} CH_2-C_6H_5\\ H_2N-CH-CONH-CH-COOCH_3\\ CH_2-COOH \end{array}$$
 (i) Identify the four functional groups.

- (ii) Write its zwitter ion structure.
- (iii) Write the structures of the amino acids obtained from the hydrolysis of aspartame.

- (iv) Which of the two amino acids is more hydrophobic?
- (b) Classify the following into monosaccharides and disaccharides:

Ribose, 2-deoxyribose, maltose, galactose, fructose and lactose.

An optically active amino acid (A) can exist in three forms depending upon the pH of the medium. If the molecular formula of (A) is  $C_3H_7NO_2$ , write

- (a) the structure of the compound in aqueous medium. What are such ions called?
- (b) in which medium will the cationic form of compound (*A*) exist?
- (c) in alkaline medium, towards which electrode, the compound (*A*) migrates in electric field?
- **36.** Answer the following:
  - (i) Which material is used as a substitute for wool in making commercial fibres such as orlon or acrilan.
  - (ii) What are the conditions required for the preparation of high density polyethene?
  - (iii) Name and give the preparation of the polymer used for making unbreakable crockery.

- (a) Account for the fact that radical polymerisation of styrene occurs in a head-to-tail manner.
- (b) Show the head to tail free radical polymerisation of the alkene  $CH_2 = C(CH_3)_2$ .
- 37. (a) Ranitidine is an antacid. Explain.
  - (b) What are food preservatives? Give one example.
  - (c) What problem arises in using alitame as artificial sweetener?

### OR

(a) Name the following compound:

- (b) What are antihistamines? Give two examples. Explain how do they act on human body?
- (c) What are the main constituents of dettol?

### SOLUTIONS

Natural rubber is prepared by polymerisation of isoprene.

$$n \, \text{CH}_{2} = \text{C} - \text{CH} = \text{CH}_{2} \xrightarrow{\text{Polymerisation} \atop (1, 4 \text{ addition})} \\
+ \text{CH}_{2} - \text{C} = \text{CH} - \text{CH}_{2} \xrightarrow{n} \\
\text{CH}_{3}$$

- 2. Vulcanisation is a process of treating natural rubber with sulphur or some compound of sulphur under heat as to modify its properties, *i.e.*, to render it non-plastic and to give greater elasticity and ductility.
- 3. Fillers such as carbon black and zinc oxide are usually added to the crude rubber before vulcanisation in order to improve its wear resistance.
- 4. Buna-S is a copolymer of butadiene and styrene.
- 5. Buna-N is a copolymer of butadiene and vinyl cyanide or acrylonitrile.
- 6. Peptide bond or peptide linkage (— CONH —)
- 7. Elastomer
- 8. Vitamin C
- 9. Alitame
- 10. Benzoyl peroxide
- 11. (a): Polymerisation takes place either by condensation or by addition reaction.
- 12. (c): Magnesium hydroxide, Mg(OH)<sub>2</sub> is a common antacid.

13. (c) : 
$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{H^+} nC_6H_{12}O_6$$
  
Cellulose D-glucose

Cellulose is a straight chain polysaccharide composed of D-glucose units which are joined by  $\beta$ -glycosidic linkages. Hence, cellulose on hydrolysis produces only D-glucose units.

- 14. (b): Glycogen is the reserve carbohydrate occurring mainly in the liver.
- 15. (c): Oil of winter green (methyl salicylate) is used in medicine.
- 16. (b)
- 17. (c): Sucrose is a non-reducing sugar.
- 18. (c): The drugs which act on the central nervous system and help in reducing anxiety are called tranquilizers.
- 19. (b): PHBV undergoes bacterial degradation in the environment hence, it is a biodegradable polymer.
- 20. (a)
- 21. Sugars like glucose and sucrose have —OH groups while cyclohexane and benzene do not. Thus, glucose and sucrose are capable of forming hydrogen bonds with water molecules and hence are soluble in water.
- **22.** (a) Hexamethylenediamine,  $H_2N (CH_2)_6 NH_2$  and adipic acid,  $HOOC (CH_2)_4 COOH$
- (b) Ethylene glycol, HOCH<sub>2</sub>—CH<sub>2</sub>OH and

**23. Natural polymers :** Those polymers which are found in plants and animals are called natural polymers *e.g.*, proteins, starch, etc.

**Synthetic polymers:** Polymers which are prepared artificially are called synthetic polymers *e.g.*, plastics like polythene, synthetic fibres such as (nylon 6, 6), etc.

### OF

Natural rubber is cis-polyisoprene and is obtained by 1, 4-polymerisation of isoprene units. In rubber molecule double bonds are located between  $C_2$  and  $C_3$  of each isoprene unit. These cis-double bonds do not allow the polymer chains to come closer for effective interactions and hence intermolecular forces are quite weak. Thus, natural rubber i.e., cis-polyisoprene has a randomly coiled structure and hence, shows elasticity.

24. (a) Soaps that float in water are made by beating tiny air bubbles into the product before their hardening.

**(b)** 
$$CH_3(CH_2)_{11}$$
  $-SO_3^-Na^+$ .

- **25.** The following reactions of *D*-glucose cannot be explained on the basis of its open chain structure :
- (i) D-Glucose does not react with sodium bisulphite (NaHSO<sub>3</sub>).
- (ii) It does not give 2, 4-DNP test and Schiff's test.
- (iii) The pentaacetate of *D*-glucose does not react with hydroxylamine.
- (iv) *D*-Glucose shows the phenomenon of mutarotation, *i.e.*, when its aqueous solution is kept for sometime its optical activity changes.
- (v) On reaction with 1 mole of methanol, it yields two monomethyl derivatives which are known as methyl  $\alpha$ -D-glucoside and methyl- $\beta$ -D-glucoside.

### OR

- (a) As amino acids have both acidic (carboxyl group) and basic groups (amino group) in the same molecule, they react with both acids and bases. Hence, they show amphoteric behaviour.
- (b) In  $\alpha$ -helix structure, intramolecular H-bonding takes place whereas in  $\beta$ -pleated structure, intermolecular H-bonding takes place.
- 26. (a) If excess of sleeping pills are taken, they may lead to death, therefore they should be taken after consultation with the doctor. Secondly, they are habit forming, therefore, they must be stopped when doctor advises the same.
- (b) Tranquilizers are used in sleeping pills.

27. Reactivity of an alkene towards cationic polymerisation increases as the stability of intermediate carbocation formed increases. The stability of carbocations increase in the following order.

$$H_3C - \overset{\dagger}{C}HCOOCH_3 < H_3C - \overset{\dagger}{C}H - Cl$$
  
 $< CH_3 - \overset{\dagger}{C}H - CH_3 < CH_3 - \overset{\dagger}{C}H - C_6H_5$   
Therefore, the reactivity of the corresponding alkene towards cationic polymerisation increases as:  
 $H_2C = CHCOOCH_3 < CH_2 = CHCl$ 

$$< CH2 = CHCH3 < CH2 = CHC6H5$$

28. (a) (i) No, a stable carbocation is not formed.

(ii) Polyvinyl alcohol can form H-bond with water hence, it is soluble in water.

OR

(a) Nucleotides are monomeric units of nucleic acids.

A nucleotide is made up of sugar, heterocyclic nitrogenous base and phosphate group.

In case of the DNA nucleotide, the sugar is *D*-2-deoxyribose whereas in RNA nucleotide, it is *D*-ribose. They also differ with respect to one base, DNA contains thymine whereas RNA contains uracil.

- (b) In a solid state, amino acids exist as dipolar ions. Therefore, melting point and solubility in water of amino acids are generally higher than that of the corresponding halo acids.
- **30.** (a) (i) Bithional is added in soap to impart antiseptic properties and to reduce the odour produced by bacterial decomposition of organic matter on skin.
- (ii) Soaps are sodium or potassium salts of long chain fatty acids which can be decomposed by microorganisms

while detergents are sodium salts of long chain alkyl hydrogen sulphate or long chain benzene sulphonic acids which cannot be decomposed by bacteria due to branching.

(b) Artificial sweeteners: The substances which provide sweetness to the food without increasing the calories to the body are known as artificial sweetening agents. These are inert and harmless and excreted from the body in urine unchanged. Saccharin and aspartame are artificial sweetening agents.

OR

(a) Substances which are added to soap to change their properties in order to make them more useful for a particular application, are called fillers. For example,

(i) Sodium rosinate, sodium silicate, borax and sodium carbonate are added to laundry soaps to increase their foaming ability.

(ii) Glycerol is added to shaving soaps to prevent them from rapid drying.

- (b) Synthetic detergents are better than soaps because they form foam even in hard water whereas soaps do not. Some of the detergents give foam even in ice cold water.
- 31. (a) The heterogeneous catalyst used for the polymerisation of ethylene is Zeigler Natta catalyst (mixture of trialkyl aluminium,  $R_3$ Al and titanium tetra-chloride, TiCl<sub>4</sub>).

$$nCH_2 = CH_2 \xrightarrow{R_3Al + TiCl_4} \leftarrow CH_2 - CH_2 \xrightarrow{R_3Al + TiCl_4}$$

(b) A polymer made by polymerisation of a single monomer is known as homopolymer and the process is known as homopolymerisation *e.g.*, polythene made by polymerisation of ethene molecules.

$$nCH_2 = CH_2 \longrightarrow -CH_2 - CH_2 / n$$
  
Ethene Polythene

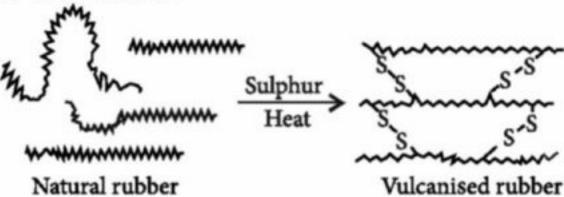
32. The significance of primary structure of proteins is that the amino acid sequence of a protein determines its function and is critical to its biological activity. Even a change of just one amino acid can drastically alter the properties of the entire protein molecule. For example change of glutamic amino acid by valine amino acid in the protein sequence causes sickle cell anaemia.

Secondary structure of proteins provide mechanical movement of muscles, bind substrates to modify them chemically. Antibody proteins bind foreign proteins. **33.** (i) Thermosetting polymer - Bakelite Thermoplastic polymer - Polythene.

(ii) Melamine-formaldehyde polymer is formed by condensation copolymerisation of melamine and formaldehyde.

(iii) Vulcanisation is a process of heating natural rubber with sulphur and an appropriate additive to modify its properties.

It gives greater elasticity and ductility. Sulphur forms cross linked network which gives mechanical strength to the rubber.



**34.** (a) Starch consists of two components, *i.e.*, amylose and amylopectin. Amylose is a linear polymer of  $\alpha$ -D-(+) glucose in which  $C_1$  of one glucose unit is connected to C<sub>4</sub> of the other glucose unit through α-glycosidic linkage. Amylopectin has similar structure but it has branched chain structure. Chain is formed by C<sub>1</sub>-C<sub>4</sub> glycosidic linkage and branching occurs by C<sub>1</sub>-C<sub>6</sub> glycosidic linkage.

Cellulose, on the other hand, is a straight chain polysaccharide composed of  $\beta$ -D-glucose and the monomeric glucose units are linked together by β-glycosidic linkage.

**(b)**  $\alpha$ -D(+)-glucose and  $\beta$ -D(+)-glucose.

(b) 
$$\alpha$$
- $D(+)$ -glucose and  $\beta$ - $D(+)$ -glucose.  
 $CH_2 - C_6H_5$ 

35. (a)  $H_2N - CH - CONH - CH - COOCH_3$ 
 $CH_2COOH$ 

Aspartame

(i) In aspartame following four functional groups are present:

(I) (-NH<sub>2</sub>) (Amine)

(II) (-COOH) (Carboxylic acid)

(ii) It's zwitter ion structure is

) It's zwitter ion structure is 
$$CH_2 - C_6H_5$$

$$H_3N^+ - CH - CONH - CH - COOCH_3$$

$$CH_2 - COO^-$$
i)

(iii) O 
$$CH_2C_6H_5$$
 $H_2N-CH-C-NH-CH-COOCH_3$ 
 $CH_2COOH$ 
 $Hydrolysis$ 
 $CH_2-C_6H_5$ 
 $H_2N-CH-COOH+H_2N-CH-COOH$ 
 $CH_2COOH$ 
 $CH_2COOH$ 
 $CH_2COOH$ 

(iv) Out of the two amino acids [i.e. (a) and (b)] formed on hydrolysis, (b) is more hydrophobic because of the presence of non-polar and bulky benzyl group.

(b) Monosaccharides: Ribose, 2-deoxyribose, galactose and fructose

**Disaccharides**: Maltose and lactose

OR

An optically active amino acid with molecular formula  $C_3H_7NO_2$  is alanine, *i.e.*,

$$\begin{array}{c} \mathbf{H_2N-CH-COOH} \\ \mathbf{CH_3} \end{array}$$

Depending upon the pH of the medium, alanine will exist in the following three forms:

$$H_3$$
N —  $CH$  —  $COOH$   $H^+$   $H_3$ N —  $CH$  —  $COO^ CH_3$   $CH_3$   $CAIIII$   $(II)$   $(II)$   $(II)$   $(III)$   $(III)$   $(IIII)$   $(IIII)$ 

- (a) In aqueous medium, alanine exists as zwitter ion (I).
- (b) In acidic medium, it will exist in cationic form (II).
- (c) In alkaline or basic medium, it exists in anionic form (III) and thus migrates towards anode under the influence of an electric field.
- 36. (i) Polyacrylonitrile, a polymer of acrylonitrile  $(CH_2 = CH - CN)$  is used in the manufacture of acrilan fibres and orlon fibres which are used as a substitute for wool.

- (ii) High density polythene is manufactured by heating ethene to 330 K-343 K under the pressure of 6-7 atm in the presence of Ziegler-Natta catalyst. The polythene thus produced practically consists of linear chains of polymer molecules. As those chains pack well, the polymer has high density.
- (iii) Melamine and formaldehyde undergo condensation copolymerisation to give melamine-formaldehyde polymer which are used to manufacture the breakresistance crockery under the brand name melmac.

OR

(a) Two radicals are formed depending on the attack of  $OR^{\bullet}$  (initiator) at the two carbon atoms linked by a double bond in styrene.

$$CH_2$$
= $CH + OR$   $CH_2$  $\dot{C}H$   $CH_2$  $\dot{C}HOR$   $CH_2$  $\dot{C}HOR$ 

Out of these two, the former is more stable being secondary and also stabilized by the phenyl ring, therefore this will control the propagation step. Its formation is also favoured by the fact that attack of  $OR^{\bullet}$  at the internal carbon atom will be sterically hindered. The stable radical will attack another styrene molecule generating a new radical.

$$ROCH_2\dot{C}H$$
 $ROCH_2-CH-CH_2-\dot{C}H-CH_2-\dot{$ 

and so on.

The process will continue. The growing polymer chain would thus be joined in a head-to-tail manner.

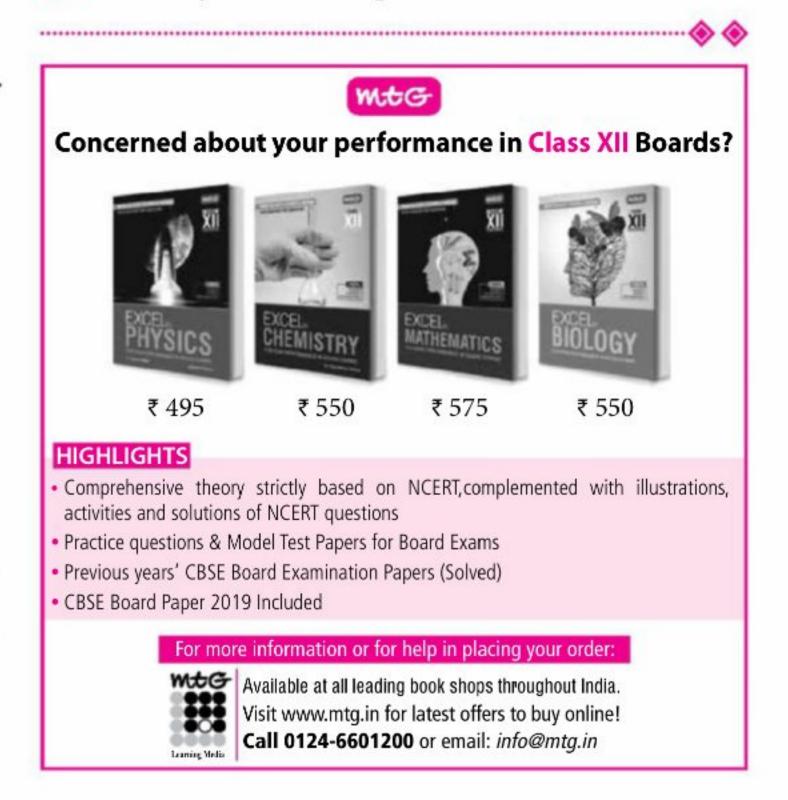
37. (a) Ranitidine is drug which suppresses the secretion of HCl, therefore, it is called antacid. The

treatment of hyperacidity came through the discovery that histamine stimulates the secretion of pepsin and hydrochloric acid. Ranitidine prevents the interaction of histamine with the receptors (inducing secretion of HCl) present in the stomach wall and thus acts as antacid.

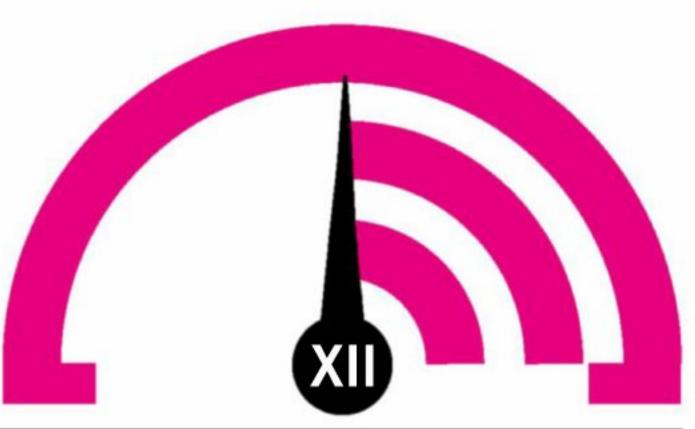
- (b) Food preservatives are those chemicals which prevent undesirable changes in flavour, colour and texture of food during storage. They delay these changes and prevent spoilage of food due to microbial growth, e.g., sodium benzoate is commonly used preservative.
- (c) Its sweetness cannot be controlled.

OR

- (a) The given structure is of bithional.
- (b) The hypersensitivity of some people towards dust, pollen grains, cat fur, a particular food, colour or fabric and certain drugs (penicillin, sulpha drugs) is called allergy. Allergy is caused due to release of a substance called histamine by the body, Antihistamines are drugs that either decrease or inhibit the action of histamine in the body, thereby, preventing allergy. Two important antihistamines or antiallergic drugs are brompheniramine and terfenadine. Histamines interact with the binding site of receptors in the body to produce allergy. Antihistamines compete with histamines for these binding sites of the receptors and thereby do not allow histamines to produce allergy.
- (c) Chloroxylenol and terpineol.



# MONTHLY TEST



his specially designed column enables students to self analyse their extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

Total Marks: 120

### **Electrochemistry | Chemical Kinetics**

Time Taken: 60 Min.

### **NEET / AIIMS**

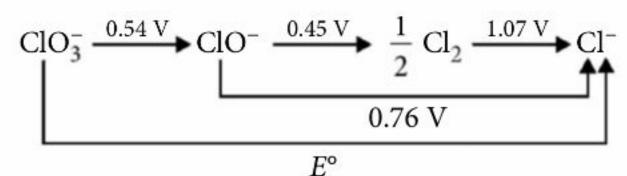
### Only One Option Correct Type

The electrode potential of a silver electrode dipped in a saturated solution of AgCl in contact with 0.1 M KCl solution at 25°C is

(Given:  $E_{Ag^+/Ag}^{\circ} = 0.799 \text{ V}$ ;  $K_{sp}$  of  $AgCl = 1 \times 10^{-10}$ )

- (a) 0.268 V (b) 0.134 V
- (c) 1.072 V
- (d) 1.33 V
- For a first order reaction  $A \rightarrow P$ , the temperature (T)dependent rate constant (k) was found to follow the equation,  $\log k = -(2000)\frac{1}{T} + 6.0$ . The preexponential factor A and the activation energy  $E_a$ , respectively, are
  - (a)  $1.0 \times 10^6 \,\mathrm{s}^{-1}$  and  $9.2 \,\mathrm{kJ \, mol}^{-1}$
  - (b) 6.0 s<sup>-1</sup> and 16.6 kJ mol<sup>-1</sup>
  - (c)  $1.0 \times 10^6 \,\mathrm{s}^{-1}$  and  $16.6 \,\mathrm{kJ} \,\mathrm{mol}^{-1}$
  - (d)  $1.0 \times 10^6 \,\mathrm{s}^{-1}$  and 38.3 kJ mol<sup>-1</sup>.
- A hydrogen electrode placed in a buffer solution of sodium cyanide and HCN in the ratio of x: y and y: x has electrode potential value a and b volts, respectively, at 25°C. If the difference a - b = 35.52 mV, then the ratio of y : x is
  - (a) 2
- (b) 5/2
- (c) 3
- (d) 2/3
- The rate constant for following reaction:  $CH_3OCH_{3(g)} \longrightarrow CH_{4(g)} + H_{2(g)} + CO_{(g)}$  at 750 K, is  $6.72 \times 10^{-3} \text{ min}^{-1}$ . Starting with a pressure of 400 mm of Hg at this temperature in a closed container, how many minutes would it take for the pressure in the container to become 760 mm Hg?

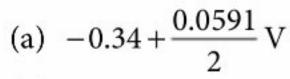
- (a) 80 min
- (b) 40 min
- (c) 89 min
- (d) 50 min
- The  $E^{\circ}(V)$  in the given figure is about



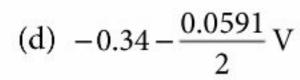
- (a) 0.55
- (b) 0.61
- (c) 0.78
- (d) 0.80
- A drop of solution (volume of 0.05 mL) contains  $3 \times 10^{-6}$  moles of H<sup>+</sup> ion. If the rate of disappearance of H<sup>+</sup> ions is  $1 \times 10^7$  mol L<sup>-1</sup> s<sup>-1</sup>, how long(s) would it take for H<sup>+</sup> ions in the drop to disappear?

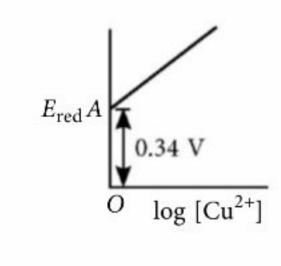


- (a)  $6 \times 10^{-6}$  (b)  $6 \times 10^{-9}$  (c)  $6 \times 10^{-2}$  (d)  $6 \times 10^{-4}$
- For the electrode,  $Cu/Cu^{2+}$ ,  $log[Cu^{2+}]$  (along *X*-axis) is plotted against  $E_{\text{red}}$  (along Y-axis). The plot obtained is shown in the figure. The electrode potential of the half cell, Cu|Cu<sup>2+</sup> (0.1 M) will be



- (b) 0.34 V
- (c)  $0.34 + \frac{0.0591}{2}$  V





Decomposition of sulphuryl chloride,  $SO_2Cl_{2(g)} \longrightarrow SO_{2(g)} + Cl_{2(g)}$ . It is found to be a first order reaction. If the initial pressure is  $P_0$  and pressure of the mixture at time t is  $(P_t)$ , then the

(a) 
$$k = \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t}$$

rate constant (*k*) would be

(b) 
$$k = \frac{2.303}{t} \log \frac{P_0 - P_t}{P_0}$$

(c) 
$$k = \frac{2.303}{t} \log \frac{P_0}{P_0 - P_t}$$

(d) 
$$k = \frac{2.303}{t} \log \frac{2P_0}{2P_0 - P_t}$$

The stability constant of the complex,  $[Zn(NH_3)_4]^{2+}$ formed in the following reaction:

$$Zn^{2+} + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{2+}$$
 is

[Given: 
$$E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76 \text{ V};$$

$$E_{[\text{Zn(NH}_3)_4]^{2+}/\text{Zn, 4NH}_3}^{\circ} = -1.03 \text{ V}$$

- (a)  $1.37 \times 10^9$  (b)  $2.35 \times 10^9$
- (c)  $3.62 \times 10^7$  (d)  $5.05 \times 10^8$
- 10. The rate constant is numerically equal for three reactions of first, second and third order respectively. Which of the following is true?

(a) If 
$$[A] > 1$$
;  $r_3 > r_2 > r_1$ 

(b) If 
$$[A] = 1$$
;  $r_1 = r_2 = r_3$ 

(c) If 
$$[A] < 1$$
;  $r_1 > r_2 > r_3$ 

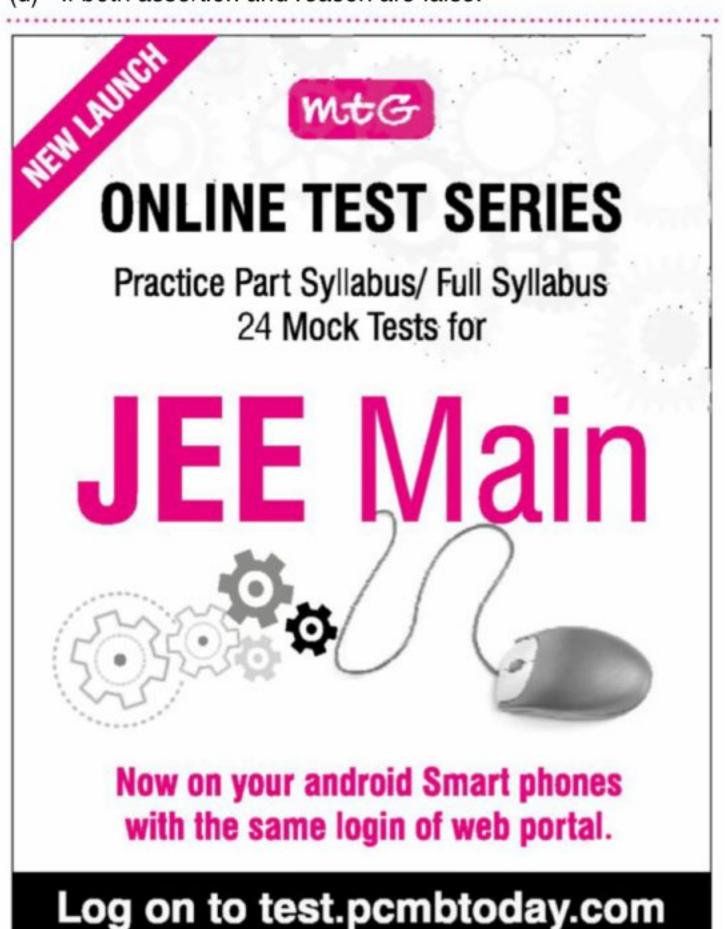
- (d) All of these
- 11. A current of 8.45 A is drawn from a Daniell cell for exactly one hour. If molar mass of Cu and Zn

- are 63.5 g/mol and 65.4 g/mol respectively, the loss in mass at anode and gain in mass at cathode respectively are
- (a) 10.0 g, 10.30 g (b) 10.30 g, 10.0 g
- (c) 16.42 g, 15.35 g (d) 10.73 g, 10.48 g
- **12.** The rate of following reaction:
  - $H_2O + 2S_2O_4^{2-}(aa) \longrightarrow 2HSO_3^{-}(aa) + S_2O_3^{2-}(aa)$  studied as follows. In an experiment, the concentration of 0.4 M  $S_2O_4^{2-}$  reduces to half in  $3.73 \times 10^6$  s. In another experiment, the concentration 0.25 M  $S_2O_4^{2-}$  reduces to half in  $6.0 \times 10^6$  s. The order of the reaction is
  - (a) first order
- (b) second order
- (c) zero order
- (d) none of these.

### Assertion & Reason Type

**Directions**: In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as:

- If both assertion and reason are true and reason is the correct explanation of assertion.
- If both assertion and reason are true but reason is not the correct explanation of assertion.
- If assertion is true but reason is false.
- If both assertion and reason are false.



**13. Assertion :** In mercury cell, the cell potential is approximately 1.35 V and remains constant during its life.

**Reason**: The overall reaction in mercury cell is represented: as  $Zn(Hg) + HgO_{(s)} \rightarrow ZnO_{(s)} + Hg_{(l)}$ 

obeys the rate expression as:  $\frac{dx}{dt} = k[A]^m [B]^n$ .

**Reason :** The rate of the reaction does not depend upon the concentration of *C*.

**15. Assertion**: If standard reduction potential for the reaction,  $Ag^+ + e^- \rightarrow Ag$  is 0.80 volt, then for the reaction,  $2Ag^+ + 2e^- \rightarrow 2Ag$ , it will be 1.60 volt.

**Reason :** If concentration of Ag<sup>+</sup> ions is doubled, the electrode potential is also doubled.

### JEE MAIN / ADVANCED

### **Only One Option Correct Type**

- 16. For a first order reaction, the ratio of the time taken for 7/8<sup>th</sup> of the reaction to complete to that of half of the reaction to complete is
  - (a) 3:1
- (b) 1:3
- (c) 2:3
- (d) 3:2
- 17. A constant current was flown for 1 min through a solution of KI. At the end of experiment, liberated I<sub>2</sub> consumed 150 mL of 0.01 M solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> following the reaction :

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

What was the average rate of current flow in ampere?

- (a) 5.25 A
- (b) 2.4125 A
- (c) 3.413 A
- (d) 4.562 A
- 18. The Arrhenius equation for the rate constant of decomposition of methyl nitrite and ethyl nitrite are

$$k_1(s^{-1}) = 10^{13} \exp\left(\frac{-152300 \text{ J mol}^{-1}}{RT}\right)$$
  
and  $k_2(s^{-1}) = 10^{14} \exp\left(\frac{-157700 \text{ J mol}^{-1}}{RT}\right)$ 

respectively. The temperature at which the rate constants are equal is

- (a) 282 K (b) 482 K (c) 582 K (d) 382 K
- 19. Copper sulphate solution (250 mL) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 minutes. It was found that after electrolysis, the absorbance of the solution was reduced to 50%

of its original value. Calculate the concentration of copper sulphate in the solution to begin with.

- (a)  $8.56 \times 10^{-5} \text{ mol L}^{-1}$
- (b)  $6.52 \times 10^{-5} \text{ mol L}^{-1}$
- (c)  $7.95 \times 10^{-5} \text{ mol L}^{-1}$
- (d)  $4.52 \times 10^{-5} \text{ mol L}^{-1}$

### More than One Options Correct Type

- **20.** The rate constant of a reaction is given by  $k = 2.1 \times 10^{10} \exp(-2700/RT)$ . It means that
  - (a) log *k* versus 1/T will be a straight line with slope =  $\frac{-2700}{2.303 R}$
  - (b) log k versus 1/T will be a straight line with intercept on log k axis =  $2.1 \times 10^{10}$
  - (c) activation energy  $(E_a)$  is equal to  $\left(\frac{-2700}{RT}\right)$
  - (d) half life of the reaction decreases with increase of temperature.
- 21. Consider the following concentration cell:

$$Zn_{(s)} | Zn^{2+} (0.024 \text{ M}) | | Zn^{2+} (0.480 \text{ M}) | Zn_{(s)}$$

Which of the following statements is(are) correct?

- (a) The EMF of the cell at 25°C is nearly 0.038 V.
- (b) The EMF of the cell at 25°C is nearly -0.038 V.
- (c) If water is added in LHS, so that the [Zn<sup>2+</sup>] is reduced to 0.012 M, the cell voltage increases.
- (d) If water is added in LHS, so that the [Zn<sup>2+</sup>] is reduced to 0.012 M, the cell voltage remains same.
- 22. For a first order reaction,
  - (a) The degree of dissociation is equal to  $(1 e^{kt})$ .
  - (b) Plot of rate *versus* concentration will be a straight line parallel to concentration axis.
  - (c) The time taken for the completion of 75% reaction is thrice the  $t_{1/2}$  of reaction.
  - (d) The pre-exponential factor in the Arrhenius equation has the dimension of time, T<sup>-1</sup>.
- **23.**  $Pt_{(s)}|Cl_2(g,1atm)|HCl(C_1)||HCl(C_2)|$

 $Cl_2(g, 1 \text{ atm}) | Pt_{(s)}$ . Mark out the correct statement(s).

- (a) Cell diagram represents electrode concentration cell.
- (b) Cell is spontaneous if  $C_1 > C_2$ .
- (c) Cell is spontaneous if  $C_1 < C_2$ .
- (d) Cell diagram represents electrolyte concentration cell.

### Numerical Value Type

- 24. A current of 1.70 A is passed through 300.0 mL of 0.160 M solution of ZnSO<sub>4</sub> for 230 sec with a current efficiency of 90%. The molarity (M) of Zn<sup>2+</sup> after the deposition of zinc is (Assume the volume of the solution to remain constant during electrolysis.)
- 25. The activation energy of a reaction is 9 kcal/mol. The increase in the rate constant when its temperature is raised from 295 to 300 K is x%. The value of x is
- **26.** For a given reaction, energy of activation for forward reaction  $(Ea_f)$  is 80 kJ mol<sup>-1</sup>.  $\Delta H = -40$  kJ mol<sup>-1</sup> for the reaction. A catalyst lowers  $Ea_f$  to 20 kJ mol<sup>-1</sup>. The ratio of energy of activation for reverse reaction before and after addition of catalyst is

### Matrix Match Type

Answer the following questions (27 and 28) by appropriately matching the columns based on the information given in the passage:

At constant temperature and volume, *X* decomposes as  $2X_{(g)} \rightarrow 3Y_{(g)} + 2Z_{(g)}$ ;  $P_x$  is the partial pressure of X.

S.No.	Time (in minute)	P (in mm of Hg)
1.	0	800
2.	100	400
3.	200	200

Column-I			Column-II
(P)	Molecularity of reaction	I.	1
(Q)	Order of reaction with respect to <i>X</i>	II.	2
(R)	Time for 75% completion of reaction	III.	$6.93 \times 10^{-3}$ min <sup>-1</sup>
(S)	Rate constant	IV.	200 min

- 27. Which of the following has the correct combination considering column-I and column-II?

  - (a)  $P \rightarrow I$  (b)  $Q \rightarrow III$
  - (c)  $R \rightarrow IV$  (d)  $S \rightarrow II$
- 28. Which of the following has the correct combination considering column-I and column-II?
  - (a)  $P \rightarrow III$
- (b)  $Q \rightarrow I$
- (c)  $R \rightarrow II$
- (d)  $S \rightarrow IV$

Answer the following questions (29 and 30) by appropriately matching the columns based on the information given in the passage:

Arrangement of metals in the order of decreasing tendency of their atoms to give electrons (i.e., undergo oxidation) is known as electrochemical series.

A metal which is placed higher up in the series will displace all metals which are kept below it from solutions of their salts.

(i) 
$$\text{Li}^+ + e^- \longrightarrow \text{Li}_{(s)}$$
;  $E_{\text{Li}^+/\text{Li}}^\circ = -3.05 \text{ V}$ 

(ii) 
$$Au^{3+} + 3e^{-} \longrightarrow Au_{(s)}$$
;  $E^{\circ}_{Au^{3+}/Au} = 1.50 \text{ V}$ 

(iii) 
$$F_{2(g)} + 2e^- \longrightarrow 2F^-$$
;  $E_{F_2/F^-}^{\circ} = 2.87 \text{ V}$ 

Column-I			Column-II		
(P)	F <sub>2</sub>	I.	Metal is the strongest reducing agent		
(Q)	Li	II.	Unreactive metal		
(R)	Li <sup>+</sup>	III.	Metal ion which is the weakest oxidising agent		
(S)	Au	IV.	Non-metal which is best oxidising agent		

- 29. Which of the following has the correct combination considering column-I and column-II?
  - (a)  $P \rightarrow III$
- (b)  $Q \rightarrow I$
- (c)  $R \rightarrow II$
- (d)  $S \rightarrow IV$
- **30.** Which of the following has the correct combination considering column-I and column-II?
  - (a)  $P \rightarrow IV$
- (b)  $Q \rightarrow II$
- (c)  $R \rightarrow I$
- (d)  $S \rightarrow III$



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SELF CHECK

Marks scored in percentage ......

Check your score! If your score is > 90%

**EXCELLENT WORK!** You are well prepared to take the challenge of final exam.

No. of questions attempted No. of questions correct

GOOD WORK! 90-75% 74-60% SATISFACTORY!

You need to score more next time.

You can score good in the final exam.

< 60% NOT SATISFACTORY! Revise thoroughly and strengthen your concepts.

# CHEMISTRY MUSING

**PROBLEM SET 77** 

nemistry Musing was started from August '13 issue of Chemistry Today. The aim of Chemistry Musing is to augment the In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / NEET. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue. We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

### JEE MAIN/NEET

1 mol of A in one litre vessel maintained at constant *T* shows the equilibrium :

$$A_{(g)} \rightleftharpoons B_{(g)} + 2C_{(g)}; K_{C_1}$$
  
 $C_{(g)} \rightleftharpoons 2D_{(g)} + 3B_{(g)}; K_{C_2}$ 

If the equilibrium pressure is  $\frac{13}{6}$  times of initial

pressure and  $[C]_{eq} = \frac{4}{9} [A]_{eq}$ , calculate  $K_{C_1}$  and  $K_{C_2}$ .

- (a) 0.11, 0.14
- (b) 2.54, 1.46
- (c) 2.96, 0.56
- (d) 5.11, 3.21
- In the given sequence of reactions,

$$CH_3Cl \rightarrow A \xrightarrow{\text{(i) conc.HNO}_3/\text{conc. H}_2SO_4, 333K} A \xrightarrow{\text{(ii) Sn/HCl}} B \xrightarrow{\text{(ii) Ac}_2O} C \xrightarrow{\text{(ii) H}_2O/H^+} C \xrightarrow{\text{(ii) NaNO}_{2(Cold)}/HCl} C \xrightarrow{\text{(iii) NaNO}_{2(Cold)}/HCl} C \xrightarrow{\text{(iii) H}_3PO_2/H}_{2O,Cu} C \xrightarrow{\text{(iii) H}_3PO_2/H}_{2O,Cu}$$

the compound D is

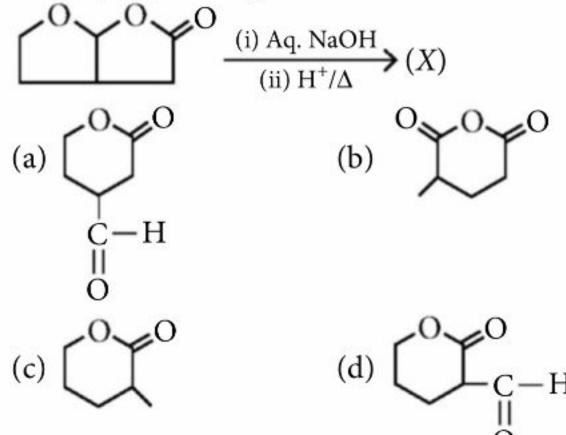
(a) 
$$O_2$$
 (b)  $O_2$   $O_2$   $O_2$   $O_2$   $O_3$   $O_4$   $O_2$   $O_4$   $O_5$   $O_5$   $O_6$   $O_7$   $O_8$   $O_$ 

- 3. A certain metal (X) is boiled in dilute HNO<sub>3</sub> to give a salt (Y) and an oxide of nitrogen (Z). An aqueous solution of (Y) with brine solution gives a white precipitate (P). When (Y) is treated with  $Na_2S_2O_3$ solution, a white precipitate (Q) is obtained which on standing turns to a black compound (R). The compound (R) formed is
  - (a) PbO
- (b) PbS
- (c)  $Ag_2S$  (d)  $Ag_2SO_3$

The gas phase decomposition of dimethyl ether follows first order kinetics.

 $CH_3OCH_{3(g)} \longrightarrow CH_{4(g)} + H_{2(g)} + CO_{(g)}$ The reaction is carried out in a container at constant volume and 500°C and has a half life of 14.5 minutes. Initially only dimethyl ether is present at a pressure of 0.40 atmosphere. The total pressure of the system after 12 minutes is (Assume ideal gas behaviour)

- (a) 0.75 atm
- (b) 0.90 atm
- (c) 0.56 atm
- (d) 0.45 atm.
- Identify (*X*) in the given reactions.





### **JEE ADVANCED**

### 6. For the following complexes:

(1) 
$$trans - [Co(NH_3)_4Cl_2]^+$$

(2) 
$$cis - [Co(NH_3)_2(en)_2]^{3+}$$

(3) 
$$trans - [Co(NH_3)_2(en)_2]^{3+}$$

(4) 
$$NiCl_4^{2-}$$
 (5)  $TiF_6^{2-}$ 

Identify the correct option(s).

- (a) (1) and (2) are optically active, (3) and (5) are optically inactive.
- (b) (2) is optically active, (1), (3) and (4) are optically inactive.
- (c) (4) is coloured, optically active and (5) is colourless, optically inactive.
- (d) (4) is optically inactive, coloured and (5) is optically inactive, colourless.

### COMPREHENSION

On ozonolysis of one mole of compound (M) gives 2 moles of glyoxal and one mole of methyl glyoxal. Compound (M) on reaction with succinic anhydride gives a compound (N) in the presence of anhydrous AlCl<sub>3</sub>. Compound (N) on heating with Zn-Hg in the presence of HCl gives compound (O). Compound (O) in the presence of conc.  $H_2SO_4$  gives compound (P) which in the presence of methyl magnesium chloride followed by hydrolysis gives compound (Q). Compound (Q) on heating in the presence of conc.  $H_2SO_4$  gives compound (R) which on heating in the presence of Se gives compound (S).

7. The compound (M) and compound (N) are respectively

(a) 
$$\bigcap_{Me}^{Me}$$
 and  $\bigcap_{Me}^{Me}$   $\bigcap_{C-CH_2-COOH}^{Me}$ 

(b) and 
$$\bigcap_{C-CH_2-COOH}^{Me}$$

(c) and 
$$C-CH_2-CH_2-CH_3$$

(d) 
$$\bigcap^{Me}$$
 and  $\bigcap^{Me}$   $C-CH_2-CH_2-COOH$ 

**8.** The compound (*S*) obtained is

$$(c) \stackrel{Me}{\longleftarrow} (d) \underset{Me}{\longleftarrow} Me$$

### **NUMERICAL VALUE**

- 9. The molar conductances at infinite dilution of AgNO<sub>3</sub>, NaCl, NaNO<sub>3</sub> are 116.5, 110.3 and 105.2 mho cm<sup>2</sup> mol<sup>-1</sup> respectively. The electrolytic conductance of AgCl in water is  $2.40 \times 10^{-6}$  mho/cm and of water used is  $1.16 \times 10^{-6}$  mho cm<sup>-1</sup>. The solubility of AgCl is  $x \times 10^{-3}$  (g litre<sup>-1</sup>). The value of x is
- 10. The total number of cyclic silicates among the following is Be<sub>2</sub>SiO<sub>4</sub> (Phenacite), ZrSiO<sub>4</sub> (Zircon), Mg<sub>2</sub>SiO<sub>4</sub> (Forsterite), Zn<sub>4</sub>Si<sub>2</sub>O<sub>7</sub>(OH)<sub>2</sub>.H<sub>2</sub>O (Hemimorphite), Sc<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> (Thortveitite), MgSiO<sub>3</sub> (Enstatite), Ca<sub>3</sub>(Si<sub>3</sub>O<sub>9</sub>) (Wollastonite), Be<sub>3</sub>Al<sub>2</sub>(SiO<sub>3</sub>)<sub>6</sub> (Beryl), Ca<sub>2</sub>Mg<sub>5</sub>(Si<sub>4</sub>O<sub>11</sub>)<sub>2</sub> (Tremolite), KAl<sub>2</sub>(OH)<sub>2</sub>(AlSi<sub>3</sub>O<sub>10</sub>)(Mica), SiO<sub>2</sub> (Quartz)

### **Solution Senders of Chemistry Musing**

Set - 76

- Kaushik Dhandekar, Nagpur Maharashtra
- Arkaprova Datta, West Bengal
- Nitun Sarkar, Kolkata

### **Solution Senders of Puzzle Corner**

- Devjit Acharjee, West Bengal, Kolkata
- Aviral Vishwakarma, New Delhi

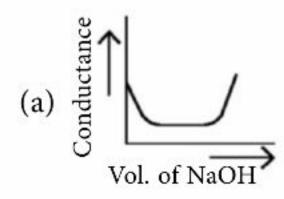


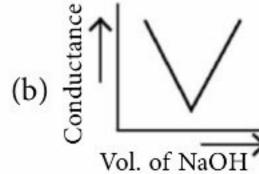
### with Numerical Value Type Questions

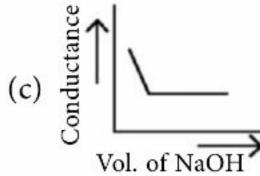
- Which of the following is inert towards potassium metal?
  - (a)
- (c)
- (d)
- Which of the following has maximum lattice energy?
  - (a) Li<sub>2</sub>O
- (b) Na<sub>2</sub>O
- (c) MgO
- (d) BaO
- Which one of the following is the correct statement?
- (a)  $B_2H_6 \cdot 2NH_3$  is known as 'inorganic benzene'.
  - (b) Boric acid is a protonic acid.
  - (c) Beryllium exhibits coordination number of six.
  - (d) Chlorides of both beryllium and aluminium have bridged chloride structures in solid phase.
- 4. x g of Zn metal was mixed with 2x g of iodine to form ZnI2. Which of the reactants will remain in excess and what fraction of it remains unreacted? (Zn = 65, I = 127)
  - (a) Zn, 0.75
- (b)  $I_2$ , 0.48
- (c) Zn, 0.48
- (d)  $I_2$ , 0.75
- **5.** For *d*-electron, the orbital angular momentum is
- (c)  $h/2\pi$
- The correct order of magnetic moments (spin only values in B.M.) is
  - (a)  $[MnCl_4]^{2-} > [CoCl_4]^{2-} > [Fe(CN)_6]^{4-}$
  - (b)  $[MnCl_4]^{2-} > [Fe(CN)_6]^{4-} > [CoCl_4]^{2-}$
  - (c)  $[Fe(CN)_6]^{4-} > [MnCl_4]^{2-} > [CoCl_4]^{2-}$
  - (d)  $[Fe(CN)_6]^{4-} > [CoCl_4]^{2-} > [MnCl_4]^{2-}$ (Atomic nos. : Mn = 25, Fe = 26, Co = 27)
- 0.0833 mol of carbohydrate of empirical formula CH<sub>2</sub>O contain 1 g of hydrogen. The molecular formula of the carbohydrate is
  - (a)  $C_6H_{12}O_6$
- (b)  $C_{12}H_{22}O_{11}$
- (c)  $C_5H_{10}O_5$
- (d)  $C_3H_4O_3$

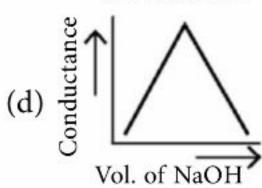
- CsCl crystallises in body-centred cubic lattice. If 'a' is its edge length then which of the following expressions is correct?

- (a)  $r_{Cs^+} + r_{Cl^-} = \sqrt{3}a$  (b)  $r_{Cs^+} + r_{Cl^-} = 3a$  (c)  $r_{Cs^+} + r_{Cl^-} = \frac{3a}{2}$  (d)  $r_{Cs^+} + r_{Cl^-} = \frac{\sqrt{3}}{2}a$
- A closed vessel contains equal number of molecules of N<sub>2</sub> and O<sub>2</sub> at a total pressure of 650 mm of Hg. If N<sub>2</sub> is completely removed, the pressure (mm of Hg) will
  - (a) drop to 650/3
- (b) drop to 650/2
- (c) remain unchanged
- (d) become  $650 \times 2$
- 10. Which of the following organometallic compound is  $\sigma$  and  $\pi$ -bonded?
  - (a)  $[Fe(\eta^5-C_5H_5)_2]$
- (b)  $[PtCl_3(\eta^2-C_2H_4)]$
- (c)  $[Co(CO)_5NH_3]^{2+}$
- (d)  $Al(CH_3)_3$ .
- 11. CH<sub>3</sub>COOH is neutralised NaOH. Conductometric titration curve will be

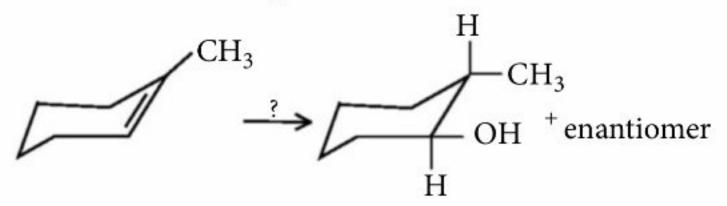








12. Which of the reagents would effect the conversion?



- (a) BH<sub>3</sub>/THF, then H<sub>2</sub>O<sub>2</sub>/OH<sup>-</sup>
- (b) H<sub>2</sub>O/Hg(OAc)<sub>2</sub>, THF then NaBH<sub>4</sub>/OH<sup>-</sup>
- (c)  $H_3O^+$ , Heat
- (d) None of these.

- 13. The correct sequence of decrease in the bond angle of the following hydrides is
  - (a)  $NH_3 > PH_3 > AsH_3 > SbH_3$
  - (b)  $NH_3 > AsH_3 > PH_3 > SbH_3$
  - (c)  $SbH_3 > AsH_3 > PH_3 > NH_3$
  - (d)  $PH_3 > NH_3 > AsH_3 > SbH_3$
- **14.** What are A, B and C in the following sequence of reaction?

B Raney Ni, H<sub>2</sub> Pt, 1 mol H<sub>2</sub> A

NaBH<sub>4</sub>, CH<sub>3</sub>OH

C

(a) in all cases

OH

in all cases

(d) 
$$A: OH$$

OH

OH

OH

- 15. Which of the following reagents is used to determine the presence of hydroxide groups in reducing sugar?
  - (a) PCl<sub>5</sub>
- (b) HIO<sub>4</sub>
- (c)  $(CH_3CO)_2O$
- (d) HI/Red P.
- **16.** Consider the following compounds:

$$Me$$
 $Br$ 
 $Me$ 
 $Me$ 
 $Br$ 
 $Me$ 
 $Br$ 
 $Br$ 
 $(A)$ 
 $(B)$ 
 $(C)$ 

The correct order of S<sub>N</sub>1 reactivity is

- (a) A > B > C
- (b) B > C > A
- (c) B > A > C
- (d) C > B > A
- 17. Which series of reactions correctly represents chemical relations related to iron and its compound?

(a) Fe 
$$\xrightarrow{O_2$$
, heat Fe<sub>3</sub>O<sub>4</sub>  $\xrightarrow{CO, 600^{\circ}C}$  FeO  $\xrightarrow{CO, 700^{\circ}C}$  Fe

(b) Fe 
$$\xrightarrow{\text{dil. H}_2\text{SO}_4}$$
 FeSO<sub>4</sub>  $\xrightarrow{\text{H}_2\text{SO}_4, O_2}$   $\xrightarrow{\text{heat}}$  Fe

(c) Fe 
$$\xrightarrow{O_2$$
, heat FeO  $\xrightarrow{\text{dil. H}_2SO_4}$  FeSO<sub>4</sub>  $\xrightarrow{\text{heat}}$  Fe

(d) Fe 
$$\xrightarrow{\text{Cl}_2, \text{ heat}}$$
 FeCl<sub>3</sub>  $\xrightarrow{\text{heat, air}}$  FeCl<sub>2</sub>  $\xrightarrow{\text{Zn}}$  Fe

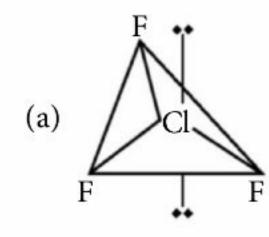
18. The major product expected from the following reaction is

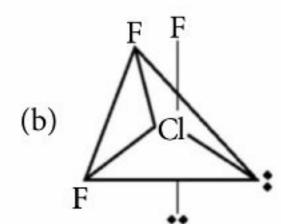
$$\begin{array}{c} \text{HOCH}_2 \text{ O} \\ \text{HO}_2\text{C} & \text{NH}_2 \\ \text{OH} \end{array}$$

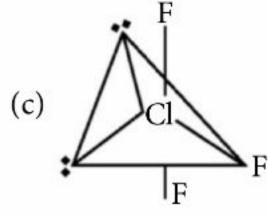
(c) 
$$HO_2C$$
 OH  $O$  OH  $O$  OH  $O$  OH

- 19. If a automobile radiator holds 1.0 kg of water, how  $many\,grams\,of\,ethylene\,glycol\,(C_2H_6O_2)\,must\,be\,add$ to get the freezing point of the solution lowered to  $-2.8^{\circ}$ C? [  $K_f$  for water is 1.86 K kg mol<sup>-1</sup>]
  - (a) 93 g (b) 39 g (c) 27 g (d) 72 g

- **20.** Which of the following structure of ClF<sub>3</sub> is most stable?







(d) All the three are of equivalent stability.

### Numerical Value Type

- 21. Sea water contains around  $6.5 \times 10^{-3}$  g of bromide ions in 1 dm<sup>3</sup>. If all the bromide ions are converted into Br<sub>2</sub> how many dm<sup>3</sup> of sea water are needed to produce 1 kg of bromine?
- 22. A reaction proceeds five times more at 60°C as it does at 30°C. The energy of activation is \_\_\_\_\_.

- 23. A compound with molecular mass 180 is acylated with CH<sub>3</sub>COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is \_\_\_\_\_.
- 24. 3-Methylpent-2-ene on reaction with HBr in presence of H<sub>2</sub>O<sub>2</sub> forms an addition product. The number of possible stereoisomers for the product is
- 25. One mole of ethanol is treated with one mole of ethanoic acid at 25°C. One-fourth of the acid changes into ester at equilibrium. The equilibrium constant for the reaction will be \_\_\_\_\_.

### **SOLUTIONS**

- 2. (c): In MgO,  $Mg^{2+}$  ion is smallest in size and has double the charge in comparison to Li<sup>+</sup> and Na<sup>+</sup> ions.
- 3. (d):
- 4. (c):  $Zn + I_2 \rightarrow ZnI_2$

Initial no. of moles  $\frac{x}{65}$   $\frac{2x}{254}$  or  $\frac{x}{127}$ 

 $I_2$  is in less amount hence  $I_2$  is the limiting reagent.

.. Zn will remain in excess.

Number of moles of Zn left unreacted =  $\frac{x}{65} - \frac{x}{127}$ 

:. Fraction of Zn remained unreacted

$$=\frac{\frac{x}{65} - \frac{x}{127}}{\frac{x}{65}} = 0.48$$

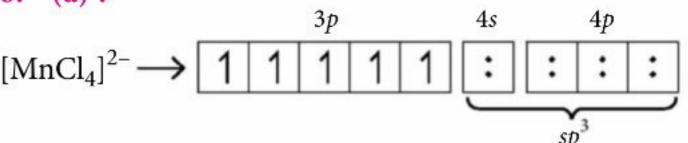
5. (a): For d-electron, l=2

Orbital angular momentum =  $\sqrt{l(l+1)} \frac{h}{2\pi}$ 

For *d*-electron orbital angular momentum

$$=\sqrt{2(2+1)}\frac{h}{2\pi}=\frac{\sqrt{6}h}{2\pi}$$

6. (a):



Number of unpaired electrons = 5

$$[\operatorname{CoCl}_{4}]^{2-} \longrightarrow \boxed{1 \hspace{-0.1cm} 1 \hspace{-$$

Number of unpaired electrons = 3

Number of unpaired electrons = 0

Magnetic moment =  $\sqrt{n(n+2)}$ 

where n = number of unpaired electrons.

i.e., greater the number of unpaired electrons, greater will be the paramagnetic character.

7. (a): 0.0833 mol of carbohydrate has 1 g hydrogen.

So, 1 mol of carbohydrate contains  $\frac{1}{0.0833}$  g of hydrogen = 12 g.

CH<sub>2</sub>O has 2 g of hydrogen.

Hence, 
$$n = \frac{12}{2} = 6$$

- .. Molecular formula of carbohydrate  $= (CH_2O)_6 = C_6H_{12}O_6$
- **8.** (d): In a body-centred cubic (*bcc*) lattice, oppositely charged ions touch each other along the cross-diagonal of the cube. In case of CsCl,  $2r_{Cs^+} + 2r_{Cl^-} = \sqrt{3}a$

or, 
$$r_{\text{Cs}^+} + r_{\text{Cl}^-} = \frac{\sqrt{3}}{2}a$$

9. (b): Equal number of molecules means equal number of moles i.e., equal mole fraction. Since, partial pressure ∞ mole fraction.

$$p_{N_2} = p_{O_2}$$

$$p_{\rm O_2} = \frac{650}{2} \, \text{mm of Hg}$$

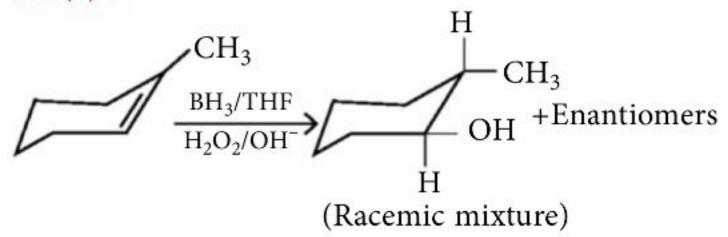
### Monthly Test Drive CLASS XII ANSWER KEY

- 1. (a) 2. (d) 3. (a) 4. (c) **5.** (b)
- 6. (b) 7. (a) 8. (a) 9. (a) 10. (d)
- 12. (b) 13. (a) 14. (a) 15. (d) **11.** (b)
- 17. (b) 18. (a) 19. (c) **16.** (a) **20.** (a,d)
- **22.** (a,d) **23.** (c,d) **24.** (0.154) **25.** (28.8) **21.** (a,c)
- **26.** (2.0) **27.** (c) **28.** (b) **29.** (b) **30.** (a)

10. (c): Metal carbonyls are  $\sigma$ - as well as  $\pi$ -bonded.

11. (a): Initially the conductance of the solution decreases because the addition of NaOH causes not only replacement of H<sup>+</sup> by Na<sup>+</sup> but also suppresses the dissociation of acetic acid but very soon conductance starts increasing with the addition of NaOH due to highly conducting OH<sup>-</sup> ions.

### 12. (a):



13. (a): Bond angle of group 15 element hydrides follows the order:

$$NH_3 > PH_3 > AsH_3 > SbH_3$$

This is due to decrease in electronegativity difference from N to Sb.

14. (d):

$$(B) \xrightarrow{\text{Raney}} O \xrightarrow{\text{Pt,}} 1 \xrightarrow{\text{mol H}_2} O \xrightarrow{\text{Pt,}} 1 \xrightarrow{\text{mol H}_2} O \xrightarrow{\text{Pt,}} O \xrightarrow{$$

15. (c): Acetic anhydride is used to determine the presence of hydroxide groups.

**16.** (b):  $S_N1$  reaction rate depends upon the stability of the carbocation, as carbocation formation is the rate determining step. Compound (B), forms a 2° allylic carbocation which is the most stable, the next stable carbocation is formed from (C), it is a 2° carbocation, (A) forms the least stable 1° carbocation, the order of reactivity is thus,

$$Me$$
 $> Me$ 
 $> Me$ 
 $> Me$ 
 $> Br$ 
 $(B)$ 
 $(C)$ 
 $(A)$ 



17. (a): Formation of  $Fe_3O_4$  through Fe, corresponds to the combustion of Fe and rest part of the reactions correspond to the production of Fe by reduction of  $Fe_3O_4$  in blast furnace.

### 18 (d):

**19.** (a) : 
$$K_f = 1.86 \text{ K kg mol}^{-1}$$

$$\Delta T_f = 0 - (-2.8) = 2.8$$
°C

Mass of solvent = 1.0 kg

Mass of solute =?

Molecular mass of solute = 62

$$\Delta T_f = K_f \times m$$

$$m = \frac{\text{Weight of solute}}{\text{Molecular mass of solute}} \times 1000$$

$$\text{Mass of solvent (g)}$$

$$m = \frac{w/62}{1000} \times 1000 = \frac{w}{62}$$

$$\Delta T_f = K_f \times m$$

$$2.8 = 1.86 \times \frac{w}{62} \implies w = \frac{62 \times 2.8}{1.86} = 93 \text{ g}$$

### 20. (c)

**21.** 
$$(307.69 \times 10^3) : Br^- \rightarrow \frac{1}{2} Br_2 + e^-$$

 $6.5 \times 10^{-3} \text{ g Br}^- = 3.25 \times 10^{-3} \text{ g Br}_2 \text{ is in } 1 \text{ dm}^3$ 

1000 g Br<sub>2</sub> is in = 
$$\frac{1000}{3.25 \times 10^{-3}}$$
 = 307.69 × 10<sup>3</sup> dm<sup>3</sup>

22. (10.76): As 
$$2.303 \log \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{T_2 - T_1}{T_2 T_1} \right)$$

Here,  $T_2 = 60 + 273 = 333$  K,

$$T_1 = 30 + 273 = 303 \text{ K}$$

$$R = 1.987 \times 10^{-3} \text{ kcal}$$
  $E_a = ?$ 

As  $r = k[A]^n$  (at a temperature T)

Hence, 
$$\frac{r_2}{r_1} = \frac{k_2}{k_1}$$
 (at temperature  $T_2$  and  $T_1$ )

but 
$$\frac{r_2}{r_1} = 5$$
 (Given)

$$\therefore \quad \frac{k_2}{k_1} = 5$$

$$\therefore 2.303 \log_{10} 5 = \frac{E_a}{1.987 \times 10^{-3}} \left[ \frac{333 - 303}{333 \times 303} \right]$$

$$\therefore E_a = 10.76 \text{ kcal mol}^{-1}$$

23. (5): No. of amino groups = 
$$\frac{390-180}{42} = 5$$

CH<sub>3</sub>

$$(4): CH_3-CH_2-C=CH-CH_3 \xrightarrow{HBr \atop H_2O_2}$$
3-Methylpent-2-ene

$$CH_{3}$$
 $CH_{3}$ 
 $C$ 

There are two chiral carbon atoms present in the product. Therefore, total number of stereoisomers are  $= 2^n = 2^2 = 4$ 

### 25. (0.11):

$$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Initially 1 1 0 0

At eqm. 
$$1 - \frac{1}{4}$$
  $1 - \frac{1}{4}$   $\frac{1}{4}$   $\frac{1}{4}$   $\frac{1}{4}$ 

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{C}_2\text{H}_5\text{OH}][\text{CH}_3\text{COOH}]} = \frac{\left(\frac{1}{4}\right)\left(\frac{1}{4}\right)}{\left(\frac{3}{4}\right)\left(\frac{3}{4}\right)} = 0.11$$

### Monthly Test Drive CLASS XI ANSWER KEY

1. (a) 2. (c) 3. (d) 4. (d) 5. (a)

6. (c) 7. (a) 8. (c) 9. (b) 10. (a)

11. (c) 12. (c) 13. (c) 14. (b) 15. (b)

**16.** (b) **17.** (a) **18.** (d) **19.** (b) **20.** (a,c,d)

**21.** (a,d) **22.** (a,b,c,d) **23.** (b,c,d) **24.** (4)

**25.** (2.64) **26.** (20) **27.** (a) **28.** (c)

**29.** (a) **30.** (c)



Dear students!! Hope you all are doing good. As the season of exams is knocking at your door, now gear up and fasten your seat belt to be safe from anxiety of lacking strategy. This is the high time that you start to revise chapter-wise and more accurately topic-wise to get into the final detailing of the subject. This time revising theory and instantly solving problems will help you a lot. This is a perfect strategy. As you all are my "bestest" friends, so like every year I am there to help you with the proper understanding of every topic with accurate problems. This issue deals with the same. Good luck!!

\*Arunava Sarkar

#### **Single Option Correct**

1. 
$$\begin{array}{c|c}
 & NH_2 & O & O \\
\hline
 & CH_3 - C - O - C - CH_3 \\
\hline
 & CH_2CH_3
\end{array}$$

$$\begin{array}{c|c}
 & NO_2Cl \\
\hline
 & NaOH CH_3OH \\
\hline
 & CH_3OH CH_3OH \\
\hline
 & CH_3OH CH_$$

Identify C' in the above sequence of reactions.

Identify the final product.

(a) 
$$O$$
 $B$ 
(b)  $O$ 
 $NH_2$ 
 $NH_2$ 
 $NH_2$ 

$$(c) \bigcirc OH \bigcirc OH \bigcirc Br$$

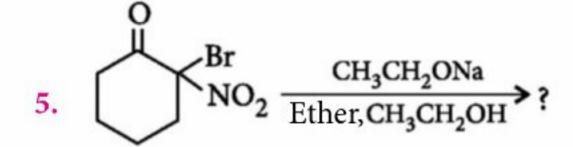
Identify the product.

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4. 
$$H_5C_2$$
 $Pb(OAc)_4 \rightarrow A \xrightarrow{H_3O^+} B$ 
 $NH_2$ 
 $dil. NaOH \rightarrow C$ 

Identify 'C' in the above sequence of reactions.

<sup>\*</sup>Institute of Chemistry (IOC)- Asansol, Durgapur, Dhanbad, Burdwan, Kolkata, Jamshedpur, Bokaro, Patna



(d) None of these

6. Cl 
$$NH \xrightarrow{1. Br_2 + KOH}$$
?

(a) 
$$Cl \longrightarrow NH_2$$
 (b)  $Cl \longrightarrow NH_3$   $\uparrow_{NH_3}$ 

(c) 
$$Cl$$
  $COOH$   $COOH$ 

7. Identify the major product in the following reaction.

Me C=N OH 
$$\frac{1. (CF_3CO)_2O}{CH_3CH_2OCH_2CH_3}$$

(c) Both (a) and (b) are major and equally formed.

**8.** Arrange the following according to their increasing order of basicity.

(a) I < II < III < IV

(b) IV < III < II < I

(c) II > II > IV > III

(d) None of these

9. 
$$\begin{array}{c|c}
Cl & & NH_3 \\
NaNO_2 & & \frac{NaNO_2}{dil. HCl} & \xrightarrow{CuCN} \\
NO_2 & & \frac{H^+/H_2O}{SOCl_2}
\end{array}$$

$$\begin{array}{c|c}
H^+/H_2O & & SOCl_2
\end{array}$$
?

Identify the final product.

Identify the final product.

(a) 
$$H_3C$$

(b)  $H_3C$ 

F

(c)  $H_3C$ 

(d) None of these

$$CH_3$$

$$CH_3C$$

Identify the product.

(a) 
$$H_3C-HC$$

NHNHC-CH<sub>3</sub>
 $CH_3$ 
 $CH_3$ 

(b)  $H_3C-HC$ 

N-COOEt

(c) 
$$H_3C-HC$$
 $N=C$ 
 $CH_2COOEt$ 
 $N=C$ 
 $CH_3$ 
 $CH_2COOEt$ 
 $CH_3$ 

(d) None of these

#### **Solutions**

–NO₂ is *meta*-directing. Hence –Br will be inserted at the *meta*-position.

3. (b): It is a mere case of Hoffmann elimination. Moist  $Ag_2O$  ( $Ag_2O + H_2O \rightarrow 2AgOH$ ) will give  $\mathbf{\ddot{O}H}$  which will abstract proton from the less hindered site. Therefore, the reaction comes out to be as below:

**4.** (c) : You know that  $Pb(OAc)_4$  gives Criegee reaction. So, the first step will be as below along with second step.

Now, in presence of dilute alkali, the product will undergoes internal aldol condensation reaction as below:

More acidic

-NH2 group is not protonated as the lone pair very much participate in resonance with the benzene ring.

7. (a): Me

C=N

$$\overrightarrow{OH}$$
 $F_3C=C-O-C-CF_3$ 
 $C=N$ 
 $\overrightarrow{OO}$ 
 $C=N$ 
 $\overrightarrow{OO}$ 
 $C=N$ 
 $\overrightarrow{OO}$ 
 $C=N$ 
 $\overrightarrow{OO}$ 
 $\overrightarrow{OO}$ 

8. (d): (I)  $sp^3$  hybridised; lone pair is involved in resonance.

(II)  $\stackrel{\ddot{N}H_2}{\bigcirc}$   $sp^3$  hybridised; lone pair is involved very much in resonance and is more than (I).

(III)  $sp^3$  hybridised; lone pair is involved in resonance  $sp^2$  hybridised; lone pair involvement in resonance is not practical.

(IV)  $sp^3$  hybridised; no question of participation of the lone pair in resonance and hence available for being protonated.

Now, in between (I) and (II), (I) is more basic as in (II), participation of the lone pair for resonance is quite high. In (III), one lone pair very much available. So, the order is, II < I < III < IV.

9. (d):  $(NH_3 + H_2S)$  converts  $-NO_2$  into  $-NH_2$ . Rest part is quite common.

$$\begin{array}{c|c}
Cl & Cl \\
\hline
NaNO_2 \\
\hline
H_2S & O \\
NH_2 & \hline
dil. HCl, 0°C-5°C \\
\hline
Diazo reaction
\\
Cl & Cl \\
\hline
NaNO_2 \\
\hline
dil. HCl, 0°C-5°C \\
\hline
Diazo reaction
\\
Cl & Cl \\
\hline
Cl & Cl \\
Cl & Cl \\
\hline
Cl & Cl \\
Cl & C$$

10. (d):
$$H_{3}C \xrightarrow{NaNO_{2}} H_{3}C \xrightarrow{NaNO_{2}} H_{3}C \xrightarrow{NO_{2}} H_{3}C \xrightarrow$$

 $NH_2$ 

COOEt

Electron donating group. This makes the lone pair of nitrogen atom attached with the benzene ring directly more available to react with the outer reagent without intervening into resonance.

without intervening into resonance.

$$CH_3 \\ H_3C - CH$$

$$CH_3 \\ CH - CH_2 \\ OH_2 \\ COOEt$$

$$NH_2 \\ A, (-H_2O), (-H^+) \\ CH_3 \\ CH - CH_2 \\ COOEt \\ NH_3C - CH$$

$$CH_3 \\ CH_3 \\ CH_3 \\ CH - CH_2 \\ COOEt \\ NH_3C - CH \\ CH_3 \\ CH_3 \\ CH_3 \\ CH_3 \\ COOEt \\ NH_3 \\ CH_3 \\ COOEt \\ NH_3 \\ CH_3 \\ CH_3 \\ COOEt \\ NH_3 \\ CH_3 \\ CH_4 \\ CH_5 \\$$

# Rank Enhancer

This column is specially designed to make your concepts crystal clear.

#### **PERIODIC PROPERTIES**

The properties which show gradual change when we move from left to right in a period and top to bottom in a group are called periodic properties.

- Atomic size: It is defined as distance between centre of nucleus of an atom to its outermost shell of electrons. It is expressed in terms of following three radius:
  - (a) Covalent radius, (b) Metallic radius,
  - (c) van der Waals' radius

It depends on following factors:

- (a) Number of shells: Atomic radius increases with increase in number of shells.
- (b) Effective nuclear charge: Atomic radius decreases with increase in effective nuclear charge.
- (c) Multiplicity of bond: Atomic radius decreases with increase in multiplicity of bonds. Example:

Molecule	CH <sub>3</sub> -CH <sub>3</sub>	$CH_2=CH_2$	СН≡СН
Covalent radius of C-atom	77 pm	67 pm	60 pm

#### Variation of atomic radii:

- (i) On moving down the group the atomic radius increases due to increase in number of shells.
- (ii) On moving left to right in a period, atomic radius decreases due to increase in effective nuclear charge.

#### **Some Deep Focus Points**

- (i) Increase in magnitude of atomic radii is more in the beginning of a group since, difference in energy between energy shells is more.
- (ii) Decrease in magnitude of atomic radii is more among representative elements than among transition elements, since electrons are added to penultimate shell.
- (iii) Small increase in atomic radii in end of a period is due to the fact that, van der Waals' radius is measured for noble gases.

  van der Waals' radius > covalent radius

 Ionisation enthalpy: It is the amount of energy required to remove most loosely bound electron from an isolated gaseous atom.

$$A_{(g)} + I.E. \longrightarrow A_{(g)}^+ + e^-$$

Successive ionisation enthalpies:

$$A_{(g)} \xrightarrow{-1e^{-}} A_{(g)}^{+} \xrightarrow{+I.E._{2}} A_{(g)}^{2+} \xrightarrow{+I.E._{3}} A_{(g)}^{3+}$$

**Units of** *I.E.* : 1 eV/atom = 23.06 kcal/mol = 96.3 kJ/mol

Factors affecting I.E.:

- (a) Atomic size :  $I.E. \propto \frac{1}{\text{Atomic size}}$
- (b) Screening effect :  $I.E. \approx \frac{1}{\text{Screening effect}}$
- (c) Effective nuclear charge : I.E. ∞ nuclear charge
- (d) Electronic configuration : fully filled > half filled > normal configuration
- (e) Penetration effect : *I.E.*  $\infty$  penetration effect and order of penetration effect is s > p > d > f

Variation of I.E.

- (i) In a period, as we move from left to right *I.E.* increases due to decrease in atomic size.
- (ii) In a group, as we move down, ionisation energy decreases due to increase in size.

**Some Deep Focus Points** 

(i) In second period,

$$I.E._1 \Rightarrow \text{Li} < \text{Be} > \text{B} < \text{C} < \text{N} > \text{O} < \text{F} < \text{Ne}$$
  
 $I.E._2 \Rightarrow \text{Li} > \text{Be} < \text{B} > \text{C} < \text{N} < \text{O} > \text{F} < \text{Ne}$ 

(ii) In third period,

$$I.E._1 \Rightarrow \text{Na} < \text{Mg} > \text{Al} < \text{Si} < \text{P} > \text{S} < \text{Cl} < \text{Ar}$$
  
 $I.E._2 \Rightarrow \text{Na} > \text{Mg} < \text{Al} > \text{Si} < \text{P} < \text{S} > \text{Cl} < \text{Ar}$ 

- (iii) Element with lowest I.E. = CsElement with highest I.E. = He
- (iv)  $Z_{eff} = Z \sigma$ , where

 $Z_{eff}$  = effective nuclear charge

Z = Actual nuclear charge

 $\sigma$  = Slater's constant (or) screening constant

Electrons in subshells	σ per electrons			
	n <sup>th</sup> shell	(n-1) <sup>th</sup> shell	(n - 2)(n -3)  etc.	
s or p	0.35	0.85	1.00	
d or f	0.35	1.00	1.00	

#### **Electron Gain Enthalpy or Electron Affinity**

Amount of enthalpy change when an electron is added to an isolated gaseous atom.

$$M_{(g)} + e^- \longrightarrow M_{(g)}^-$$
;  $\Delta_{eg}H$ 

#### Factors affecting electron affinity:

- (a) Atomic size:  $E.A. \approx \frac{1}{\text{Atomic size}}$
- (b) Effective nuclear charge :  $\Delta_{eg}H \propto Z_{eff}$
- Stability of electronic configuration: Elements having fully filled (or) half filled configuration have very low (or) zero value of  $\Delta_{eg}H$  and  $\Delta_{eg}H = +ve$ .

#### Variation of E.A.:

- Variation in period : As we move from left to right, electron affinity increases as atomic size decreases.
- (ii) Variation in group : As we move down, electron affinity decreases.

#### **Some Deep Focus Points**

- Among all elements, Cl has maximum E.A.
- (ii) Among metals, gold has high *E.A.*
- (iii) I.E. of X = E.A. of  $X^+$
- (iv) Cl > F > Br > I
- (v) S > O > P > N
- **Electronegativity**: Measure of tendency of an atom to attract shared pair of electrons towards itself.

#### Factors affecting electronegativity:

- Atomic size :  $E.N. \propto \frac{1}{\text{Atomic size}}$
- (ii) Nuclear charge : E.N. ∞ nuclear charge
- (iii) Screening effect :  $E.N. \propto \frac{1}{\text{Screening effect}}$
- (iv) %s character :  $E.N. \propto \%$  s character
- Electronegativity scales: Electronegativity is tendency not a physical quantity. Hence, scales are used to compare and for quantitative measurements.
- Pauling scale (Bond energy scale):

$$\chi_A - \chi_B = 0.1017 \sqrt{\Delta}$$
 (if  $\Delta$  in kJ/mol)  
=  $0.208 \sqrt{\Delta}$  (if  $\Delta$  in kcal/mol)  
and  $\Delta = E_{A-B} - \frac{1}{2}(E_{A-A} + E_{B-B})$ 

**Note**: (i) For reference, take  $\chi_A = 2.1$ 

- (ii) On this scale, F is found to have maximum electronegativity (= 4).
- (2) Mulliken scale:  $\chi_A = \frac{I.E. + E.A.}{2}$

$$\chi_A = \frac{I.E. + E.A.}{5.6} \text{ (if eV)} = \frac{I.E. + E.A.}{2 \times 62.5} \text{ (if kcal/mol)}$$
$$= \frac{I.E. + E.A.}{544} \text{ (if kJ/mol)}$$

Relation between Mulliken and Pauling scale:

$$\Rightarrow \chi_{\text{Pauling}} = \frac{\chi_{\text{Mulliken}}}{2.8}$$

$$\Rightarrow \chi_{\text{Pauling}} = \frac{\chi_{\text{Mulliken}}}{2.8}$$
(3) Allred-Rochow scale:  $E.N. = \frac{0.359 \times Z_{\text{eff}}}{r^2} + 0.744$ 

 $r = \text{covalent radius}, Z_{eff} = \text{effective nuclear charge}$ 

#### Variation of electronegativity:

- As we move from left to right in a period, electronegativity increases.
- (ii) As we move down the group, electronegativity decreases.

#### **Summary of Variation of Periodic Properties**

	Periodic property	Down the group	Left to right in period
1.	Atomic size	Increases	Decreases
2.	Ionisation enthalpy	Decreases	Increases
3.	Electron affinity	Decreases	Increases
4.	Electronegativity	Decreases	Increases
5.	Metallic nature	Increases	Decreases
6.	Acidic nature of oxides	Decreases	Increases
7.	Valency	Constant	First increases then decreases
8.	Reducing ability	Increases	Decreases

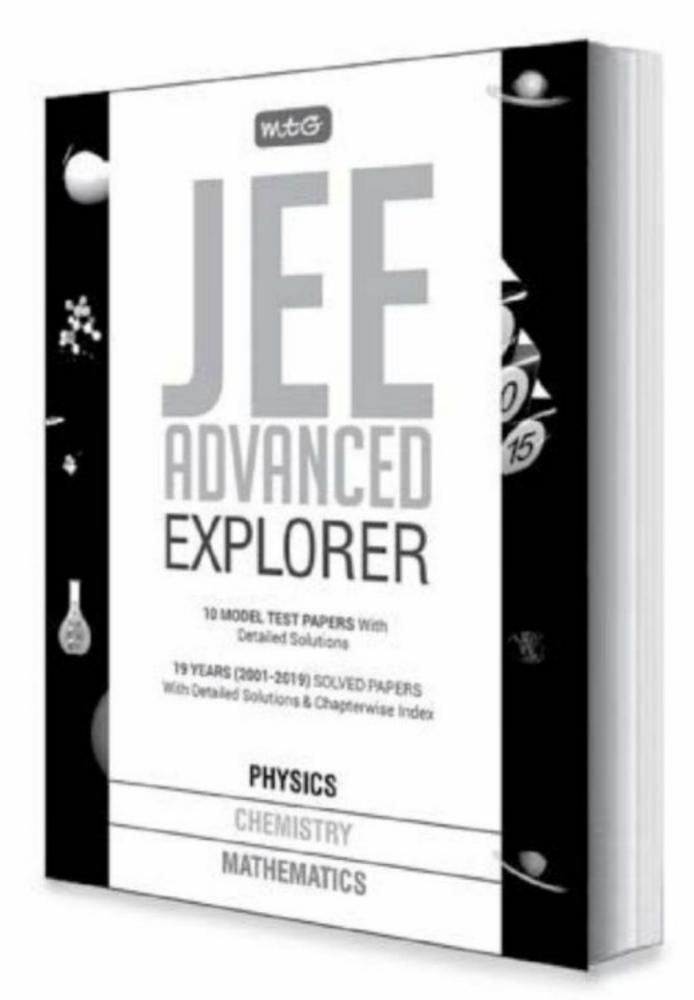
#### QUESTIONS FOR PRACTICE

#### **Single Option Correct Type**

- If first three successive ionisation energies of an element A are 520, 7297 and 11810 kJ mol<sup>-1</sup> respectively, element belongs to
  - (a) group 15
- (b) group 18
- (c) group 1
- (d) group 2.
- Most basic oxide among the following is
  - (a) SiO<sub>2</sub> (b) Na<sub>2</sub>O (c) CO<sub>2</sub> (d) SO<sub>2</sub>
- In inert gases, element with highest electron gain enthalpy is
  - (a) He
- (b) Ne
- (c) Rn
- (d) all have same.

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- Mass fraction of hydrogen in hydride of 14th group element is 0.125. Then the formula of hydride is (a) CH<sub>4</sub> (b) GeH<sub>4</sub> (c) SiH<sub>4</sub> (d) SnH<sub>4</sub>
- Which of the following electronic configuration corresponds to maximum electron affinity?

- (a)  $1s^2 2s^2 2p^5$  (b)  $1s^2 2s^2 2p^6 3s^2 3p^5$  (c)  $1s^2 2s^2 2p^3$  (d)  $1s^2 2s^2 2p^6 3s^2 3p^3$
- The ionic radii (in Å) of  $N^{3-}$ ,  $O^{2-}$  and  $F^{-}$  respectively are
  - (a) 1.71, 1.40, 1.36 (b) 1.71, 1.36, 1.40
  - (c) 1.36, 1.40, 1.71 (d) 1.36, 1.71, 1.40
- Electronegativity of Be is nearly equal to
- (a) B
- (b) Mg (c) Al (d) Si

- If configurations of elements P, Q, R, S are  $P \to 1s^2 \ 2s^2 \ 2p^6$   $Q \to 1s^2 \ 2s^2 \ 2p^6 \ 3s^1$   $R \to 1s^2 \ 2s^2 \ 2p^4$   $S \to 1s^2 \ 2s^2 \ 2p^5$ Correct order of electron accepting tendency is

  - (a) P < R < Q < S (b) P < Q < R < S

  - (c) S < R < Q < P (d) S < Q < R < P
- If bond energies of A A, H H and H A are 38, 104 and 138 kcal/mol respectively, electronegativity of A is
  - (a) 3.5 (b) 3.8 (c) 3.0 (d) 1.7

- 10. Which of the following is not a fixed quantity for an element?
  - (a) *I.E.*<sub>1</sub>
- (b) *E.A.*
- (c) Electronegativity (d) I.E.2

#### **Matching List Type**

11. Match the following:

Electronic configuration		Electron gain enthalpy		
(A)	$1s^2 \ 2s^2 \ 2p^6 \ 3s^1$	(P)	-328	
(B)	$1s^2 \ 2s^2 \ 2p^5$	(Q)	-141	
(C)	$1s^2 \ 2s^2 \ 2p^4$	(R)	-53	
(D)	$1s^2 2s^2 2p^6$	(S)	+48	

**12.** Match the following:

Element		Slater's constant		
(A)	Be	(P)	4.15	
(B)	Na	(Q)	2.05	
(C)	Ne	(R)	1.70	
(D)	Li	(S)	8.80	

#### **Hints & Solutions**

1. (c): As  $I^{st}$  ionisation energy of A is very low, it can't belong to 15, 16 groups and there is sudden increase in  $I.E_2$ . Hence, it belongs to group 1.

- (b): Metal oxides are basic and non-metal oxides are acidic. In given oxides, Na being most metallic, Na<sub>2</sub>O is most basic.
- 3. (b): He < Rn < Xe < Kr = Ar << Ne (+48) (+68) (+77) (+96) (+96) (+116)
- 4. (c): For 14<sup>th</sup> group, valency will be 4 hence general formula will be  $AH_4$ . Let mass of A = m.

Then mass fraction of H =  $\frac{(4\times1)}{(4\times1)+(m\times1)}$  = 0.125

$$m = 28$$

Atomic mass of Si = 28 : Formula is  $SiH_4$ .

(b): In options (c) and (d), elements belong to 15<sup>th</sup> group whereas in options (a) and (b) elements belongs to  $17^{th}$  group. E.A. of  $17^{th}$  group > 15th group and option (b) corresponds to Cl, (a) corresponds to F.

As  $(E.A)_{Cl} > (E.A)_F$  therefore, option (b) is correct.

6. (a):

	$N^{3-}$	O <sup>2-</sup>	F-
Electrons	10	10	10
Protons	7	8	9

No. of protons per  $10e^-$  increases

- :. Effective nuclear charge increases and ionic radius decreases.

Be shows diagonal relationship with Al.

- **(b)**: P < Q < RInert gas Metal Chalcogen Halogen
- 9. **(b)**:  $\Delta = 138 \frac{1}{2}(38 + 104) = 67$

$$\chi_A - \chi_H = 0.208 \sqrt{67}$$
 $\chi_A - 2.1 = 0.208 \sqrt{67} \implies \chi_A = 3.8$ 

- 10. (c): Electronegativity is a tendency but not quantity.
- 11. A  $\rightarrow$  R, ; B  $\rightarrow$  P, ; C  $\rightarrow$  Q, ; D  $\rightarrow$  S

Halogens have more -ve EGE. Metals have less -ve EGE and noble gases has +ve EGE.

12. A  $\rightarrow$  Q, ; B  $\rightarrow$  S, ; C  $\rightarrow$  P, ; D  $\rightarrow$  R Be  $\Rightarrow 1s^2 2s^2 = (2 \times 0.85) + 1 \times 0.35 = 2.05$ Na  $\Rightarrow$  1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>1</sup> = (2 × 1) + (0.85 × 8) = 8.80 Ne  $\Rightarrow$  1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> = (2 × 0.85) + (7 × 0.35) = 4.15  $Li = 1s^2 2s^1 = (0 \times 0.35) + (2 \times 0.85) = 1.70$ 



## How to overcome exam stress and anxiety

Exams whether of school, Board or of any competition like NEET, AIIMS, JEE, etc. have grown into a do or die pressure-giving event which makes students go through a lot of stress and anxiety. This can cause major mental health issues if allowed to develop. The fear of these exams casts dire consequences on students. The time which the students could have used in having a focused preparation goes wasted in worrying for the exams. Hence, the solution to this problems lies in systematic planning followed by actually making the plan work by following it.

#### Here are some tips to get rid of exam fear and anxiety:

#### Plan an early revision

By now, students might have completed their curriculum and started revision. Practice, practice and do more practice by solving as much as questions and problems related to your subjects.

#### Plan a productive timetable

To start for a result-oriented preparation, formulation of a productive timetable is extremely necessary. Hence, the subjects that the students consider lesser prepared, would rule their timetable. The students give more time to these disciplines. Draw plan for each day and each week. During their daily study, things like inclusion of breaks and their duration, addressing their other important jobs etc, will need students regulate them on daily basis. Hence, students must prepare themselves to deal with these each day.

Also, students may try sticking to a schedule of fixing a few days or a week for each of their subjects. The approach will likely help them to complete their preparation in a timely manner.

#### Consider incorporation of more subjects into daily studies

Preparing for a single subject for hours and hours may get quite monotonous for students. Hence, they can consider extending their devotion to a few more subjects in a single day.

#### Prepare notes

Preparing notes while studying will help the students immensely. These

would provide them the facility of getting support as and when they desire.

Try to make notes of important facts, formulae, unit conversions in the form of table, flowcharts, etc.

Moreover, students can also use a highlighting pen for attracting their attention to words/phrases or (parts of) sentences they need to prepare, more quickly.

#### Practice solutions to question papers of previous years

Following such an exercise will provide the students the opportunities for refining their concepts. It will indicate their stand for the upcoming exams. The questions and problems in these papers will provide them almost the same environment as the actual exams will provide them. This is because they will reflect the same pattern as will be there in the exams. Furthermore, students can turn their study-room into a real exam-room if they stipulate their preparation with the general 3-hour limit. Such an arrangement would really provide them almost real outcomes regarding their preparation.

MTG Previous Years' Questions Bank and Mock Test Papers series of various exams will be very helpful for students.

#### Schedule regular breaks, have a balanced meal and sleep well

The students must consider the size, number and the ways to spend their breaks, when giving breaks to their preparation. They can fully avail this liberty here! They must only be mindful of the fact that they need to maintain a good balance between their breaks and study session. The duration of the sleep may depend on requirements from student to student. Still, a 7-hour slumber would be an ideal one. Students must take a healthy meal filled with all the necessary five nutrients- protein, carbohydrates, fats, minerals, and vitamins.

Students must not compromise with the outcomes of their efforts on preparation, come what may! So, keep the stress aside, and get down to work!

All the Best! 💍



## CHEMISTRY MUSING

#### **SOLUTION SET 76**

1. (d): Reactions take place at electrodes are:

At cathode:  $AuCl_4^- + 3e^- \longrightarrow Au + 4Cl^-$ 

At anode:  $Cl^- \longrightarrow \frac{1}{2} Cl_2 + e^-$ 

For the deposition of 197 g (1 mole) of Au = 3F of charge is required thus, for the deposition of 78 g of

Au, charge required =  $\frac{3}{197} \times 78 = 1.19$  F

 $= 1.19 \times 96500$  coulombs

From  $Q = I \times t$ 

$$t = \frac{Q}{I} = \frac{1.19 \times 96500}{6} = 19139.16 \text{ sec}$$

By 1 F charge, 35.5 g of Cl<sub>2</sub> gas is formed, thus from 1.19 F, mass of chlorine gas formed =  $35.5 \times 1.19$ = 42.24 g

2. (a): Mass of electron =  $\frac{1}{1835}$  × Mass of proton

K.E. of electron = 16E

Mass of proton =  $m_p$ 

K.E. of proton = 4E

Mass of  $\alpha$ -particle =  $4m_p$ 

*K.E.* of  $\alpha$ -particle = E

$$\lambda_e = \frac{h}{\sqrt{2\left(\frac{m_p}{1835}\right) \times 16E}} = \frac{h\sqrt{1835}}{4\sqrt{2 \times m_p E}}$$

$$\lambda_p = \frac{h}{\sqrt{2 \times m_p \times 4E}} = \frac{h}{2\sqrt{2m_p E}}$$

$$\lambda_{\alpha} = \frac{h}{\sqrt{2 \times 4m_p \times E}} = \frac{h}{2\sqrt{2m_p E}}$$

$$\lambda_e > \lambda_p = \lambda_{\alpha}$$

(Y)

(d): Heat of hydrogenation depends upon number of  $\pi$ -bonds. When number of  $\pi$ -bonds are same then stability of the compound depends upon the number of alkyl group attached to doubly bonded carbon atom. Greater the number of alkyl group more stable is the alkene.

Heat of hydrogenation  $\propto \frac{1}{\text{Stability of compound}}$ 

(a,d): Assume 1 F charge is passed through FeSO<sub>4</sub>,  $Fe_2(SO_4)_3$  and  $Fe(NO_3)_3$ .

 $FeSO_4$   $Fe_2(SO_4)_3$  $Fe(NO_3)_3$ 

 $\frac{56}{2}$   $\frac{56}{3}$ Amount of Fe deposited

(a): The reaction for the formation of pentane is  $5C_{(s)} + 6H_{2(g)} \longrightarrow C_5H_{12(g)}$ 

For *n*-pentane :

 $\Delta_r H^\circ = \Delta_f H^\circ (n\text{-pentane}) - 5\Delta_f H^\circ(C_{(s)}) - 6\Delta_f H^\circ(H_{2(g)})$ 

 $\Delta_r H^{\circ} = -200 \text{ kJ/mol}$ 

For *n*-pentane :  $\Delta_r S^{\circ}$ 

$$= \Delta_f S^{\circ}(n\text{-pentane}) - 5\Delta_f S^{\circ}(C_{(s)}) - 6\Delta_f S^{\circ}(H_{2(g)})$$

or 
$$\Delta_r S^\circ = 360 - 5 \times 6 - 6 \times 130 = 360 - 810$$
  
=  $-450 \text{ J K}^{-1} \text{ mol}^{-1}$ 

$$\Delta_r G^{\circ} = \Delta_r H^{\circ} - T \Delta_r S^{\circ} = -200 + 400 \times 0.450$$
$$= -20 \text{ kJ/mol}$$

(d):  $5C_{(s)} + 6H_{2(g)} \longrightarrow C_5H_{12(g)}$ 

(Mixture of *n*-pentane, *iso*-pentane and *neo*-pentane)

$$\therefore \quad \text{For } n\text{-pentane, ln } K_{eq_1} = -\frac{\Delta_r G^{\circ}}{RT} = \frac{20}{RT}$$

 $K_{eq_1} = e^{20/RT}$ 

For *iso*-pentane,  $K_{eq_2} = e^{\frac{22}{RT}}$  and For neo-pentane,  $K_{eq_3}^{12} = e^{26/RT}$ 

: 
$$K_{eq_1} = \frac{p_n}{p_{H_2}^6}$$
 :  $p_n = K_{eq_1} \times p_{H_2}^6$ 

and  $p_{\text{iso}} = K_{eq_2} \times p_{\text{H}_2}^6$  and  $p_{\text{neo}} = K_{eq_3} \times p_{\text{H}_2}^6$ 

At equilibrium,

$$x_{\text{neo}} = \frac{K_{eq_3}}{K_{eq_3} + K_{eq_2} + K_{eq_1}} = \frac{1}{1 + \frac{K_{eq_2}}{K_{eq_3}} + \frac{K_{eq_1}}{K_{eq_3}}}$$

9. (6): Mass of Fe<sub>2</sub>O<sub>3</sub> in the given sample 
$$=\frac{55.2}{100} \times 1$$
  
= 0.552 g

Number of moles of 
$$Fe_2O_3 = \frac{0.552}{159.8} = 3.454 \times 10^{-3}$$

(Mol. wt. of 
$$Fe_2O_3 = 159.8$$
)

1 mole of Fe<sub>2</sub>O<sub>3</sub> will give 2 moles of Fe<sup>3+</sup>

$$= 2 \times 3.454 \times 10^{-3}$$
 moles of Fe<sup>3+</sup>

$$= 6.908 \times 10^{-3} \text{ mol} = 6.908 \text{ mmoles}$$

Fe<sup>3+</sup> is reduced to Fe<sup>2+</sup> by zinc dust.

Since the conversion of Fe<sup>2+</sup> to Fe<sup>3+</sup> or Fe<sup>3+</sup> to Fe<sup>2+</sup> involves only 1 electron change, so the molecular weight is same as equivalent weight.

Amount of  $Fe^{2+}$  ion in 100 mL of solution = 6.908 meq. Volume of oxidant used for 100 mL of  $Fe^{2+}$  solution

$$= 17 \times 4 \text{ mL} = 68 \text{ mL}$$

Amount of oxidant used =  $68 \times 0.0167$  mmoles = 1.1356 mmoles Let, the number of electrons taken up by oxidant = nNumber of meq of oxidant used =  $1.1356 \times n$ 

Thus, 
$$1.1356 \times n = 6.908$$
 or  $n = \frac{6.908}{1.1356} \approx 6$ 

1.1356

10. (4): 
$$A_4 + O_2 \longrightarrow B$$

Initial moles 0.375 1 0

Final moles 0 0  $x$ 

Since pressure after reaction is half of the initial pressure so after reaction gaseous moles,  $x = \frac{1}{2}$ 

i.e. 
$$\frac{1}{2}$$
 mole of B is formed.

Now the number of moles of oxygen atoms before and after reaction = 2 moles

- $\Rightarrow$  0.5 moles of B contains = 2 moles of O atoms
- $\Rightarrow$  1 mole of *B* contains = 4 moles of O atoms 1 molecule of *B* contains = 4 atoms of oxygen



## More than half of South Asian youth are not on track to have the education and skills necessary for employment in 2030: UNICEF

An estimated 54 per cent of South Asian youth leave school without the necessary skills to get a decent job in the next decade, according to data produced by the Global Business Coalition for Education (GBC-Education), the Education Commission, and UNICEF. According to the data, South Asia lags behind several other regions in preparing the next generation of young people with the skills they will need for 21st century work. Projections place South Asia well below the global average. This builds on the estimates UNICEF produced with the Commission last year on the projected learning outcomes in 2030 for all South Asian countries.

"Every day, nearly 100,000 young South Asians – a large sports stadium of young people – enter the labour market, almost half of them not on track to find 21st century jobs," said Henrietta Fore, UNICEF Executive Director. "South Asia is at a critical juncture, with a limited window during which it can reap significant demographic dividends from its talented and capable youth. Get it right, and millions could be lifted out of poverty. Fail to do so, and economic

Children in South Asia on Track to Complete Secondary School & Learn Basic Skills by 2030\*

Based on current trends

Million	Today	2030 Projection	School-Age Children in 2030	
(0)	†	†	13.9 Million	
Bangladesh 🔳	26%	55%	37.8 Million	
Bhutan 💹	47%	81%	0.2 Million	
-	19%	47%	309.6 Million	
Maldives 🔲	16%	46%	0.09 Million	
Nepal 🔃	13%	46%	7.1 Million	
Pakistan C	18%	40%	64.3 Million	
Sri Lanka	61%	68%	3.8 Million	

<sup>†</sup> Afghanistan is not included due to lack of recent learning assessment data at the secondary level.

growth will falter, youth despair will rise, and further talent will be lost to other regions." With almost half of its population of 1.8 billion below the age of 24, led by India, Pakistan and Bangladesh, South Asia will have the largest youth labour force in the world until 2040. This offers the region the potential to drive vibrant and productive economies. If strong investments in skills development are made, the region is poised to maintain strong economic growth as well as an expansion of opportunities in the education and skills sectors in the coming decades.

However, a recent UNICEF 'Voices of Youth' survey conducted among 32,000 young people in South Asia reveals concerns among these under 24-year-olds about how well they are being prepared for the modern economy. According to the poll, many young people in South Asia feel their education systems are outdated and do not prepare them for employment. They cite lack of work experience (26%), inadequate support services to improve employability (23% received no support and most received limited and not comprehensive support), and bribery demands/discriminatory and unfair hiring practices (44%) as key barriers to finding employment even after they have graduated.

"This is a crisis," said Justin Van Fleet, Executive Director of the Global Business Coalition for Education. "Addressing the youth skills gap in South Asia requires government investments, commitments from the business community, contributions from civil society, and the perspective of young people to best equip the next generation to successfully enter the rapidly changing job market." A separate new report commissioned by UNICEF identified major obstacles to addressing the youth skills gap in the region. These include the low quality of education and suboptimal vocational training which do not give students the desired skill levels the labour market demands, among others. Compiled by Ernst & Young India, this report identifies a total of 30 already-in-operation solutions to the youth skills crisis.

<sup>\*</sup> These estimates were generated based on a 2019 update of the Education Commission's original 2016 projections model for the Learning Generation report. Most recent national learning assessment data used for each country as follows: BCSE 2015 for Bhutan, GCE O Levels 2016 for Sri Lanka, LASI 2015 for Bangladesh, NAT 2016 for Pakistan, NCERT 2017 for India, Nepali country assessment 2017 for Nepal, O Level Exam 2016 for Maldives. Afghanistan is not included due to lack of recent learning assessment data at the secondary level.



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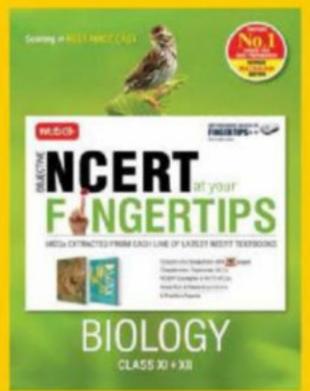
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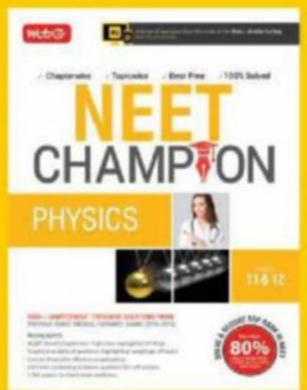


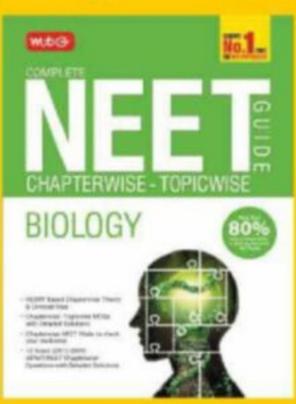
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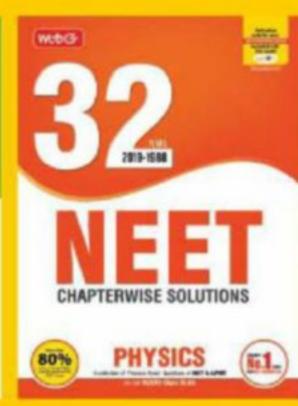
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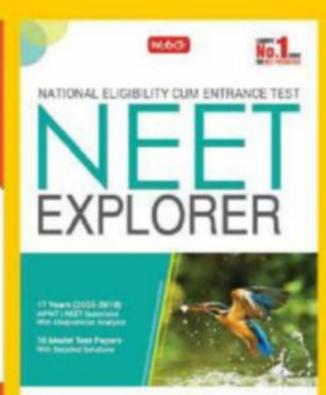
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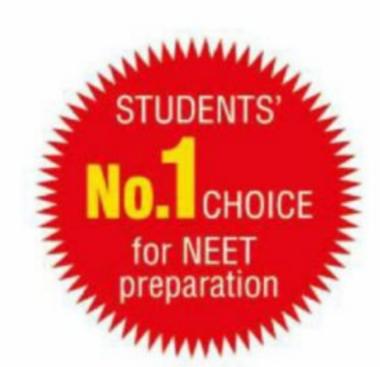


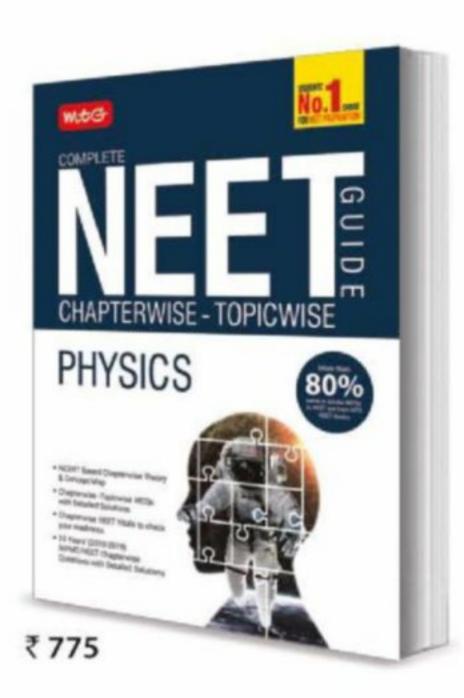
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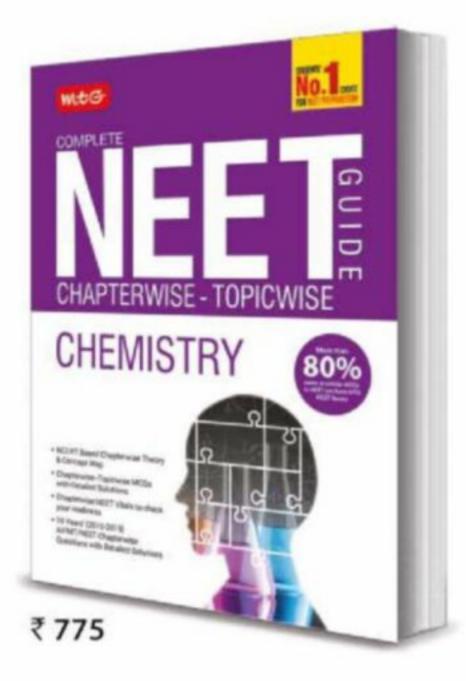


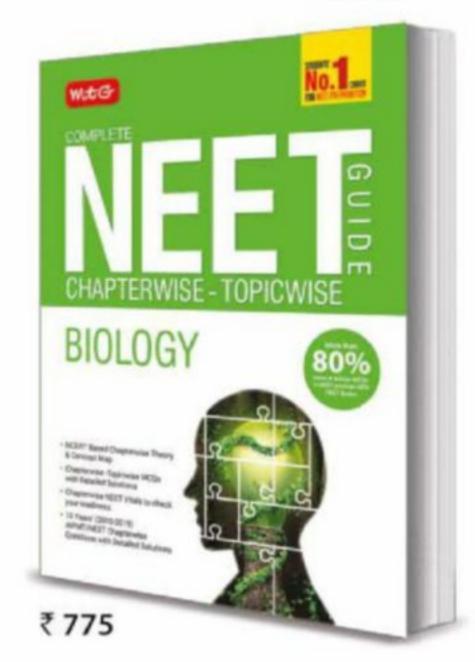


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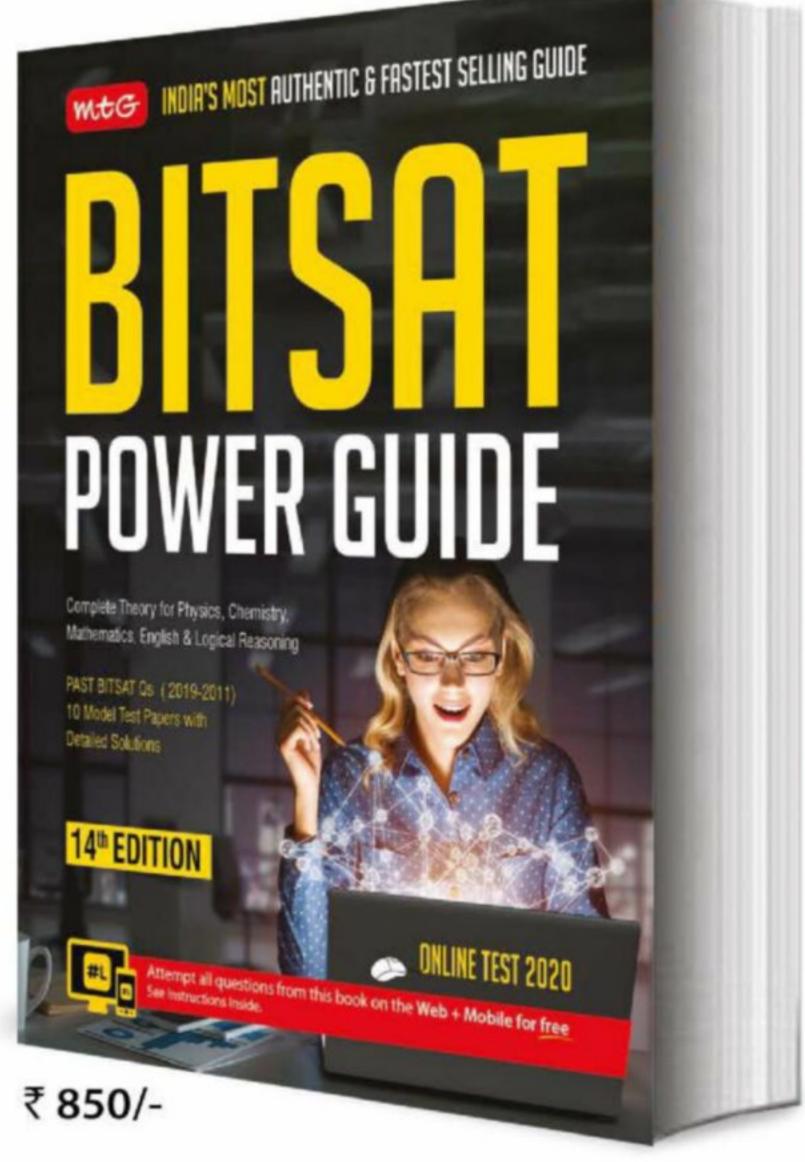




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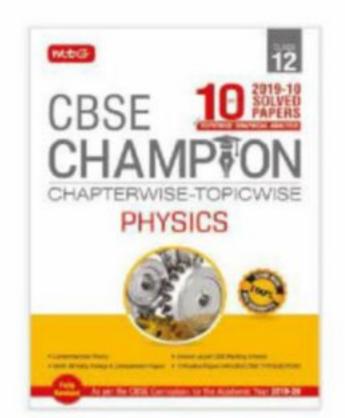
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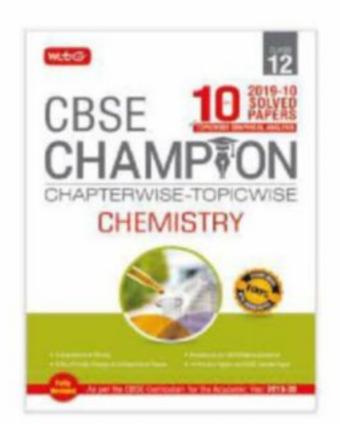
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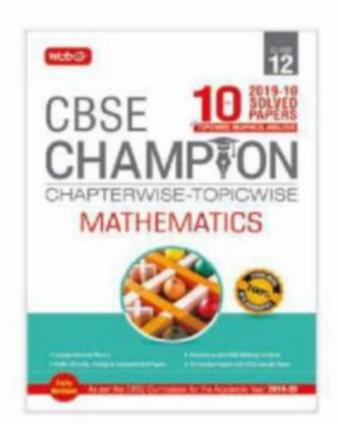
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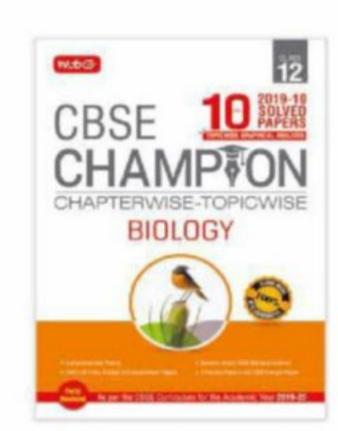


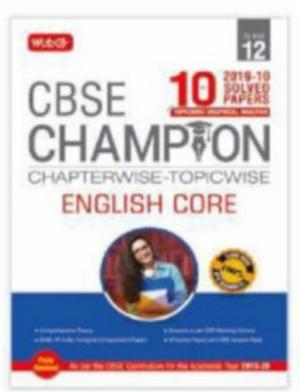
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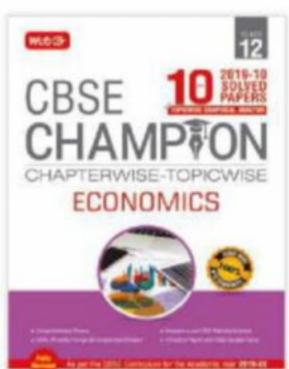


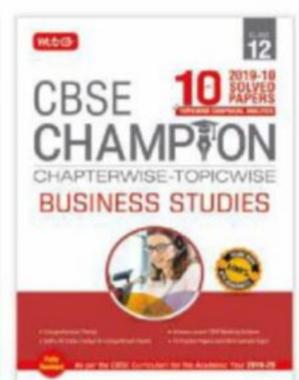


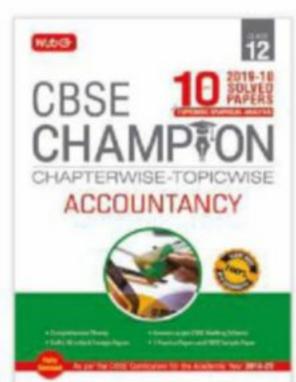


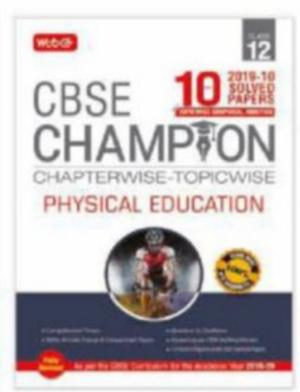


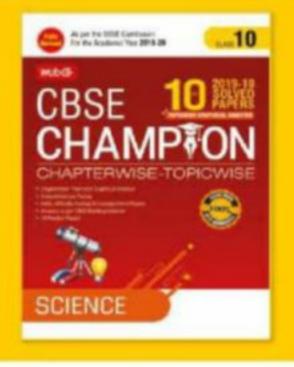




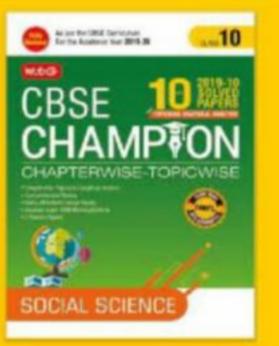
















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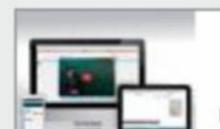
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